OCT 1 9 1925

Library

JOURNAL

OF

THE CHEMICAL SOCIETY

CONTAINING

PAPERS COMMUNICATED TO THE SOCIETY

1925, VOL. 127, SEPTEMBER

President:

ARTHUR W. CROSSLEY, C.M.G., C.B.E., D.Sc., F.R.S.

Vice-Presidents

WHO HAVE FILLED THE OFFICE OF PRESIDENT:

H. E. ARMSTRONG, LL.D., Ph.D., F.R.S.
W. H. PERKIN, Sc.D., LL.D., F.R.S.
Sir W. J. POPE, K.B.E., LL.D., F.R.S.
ALEXANDER SCOTT, M.A., D.Sc., F.R.S.
Sir JAMES WALKER, LL.D., F.R.S.
W. P. WYNNE, D.Sc., F.R.S.

Vice-Presidents:

J. B. COHEN, D.Sc., Ph.D., F.R.S.
A. J. GREENAWAY, F.I.C.
G. T. MORGAN, O.B.E., D.Sc., F.R.S.
JAMES C. PHILIP, O.B.E., D.Sc., F.R.S.
N. V. SIDGWICK, M.A., Sc.D., F.R.S.
J. M. THOMSON, LL.D., F.R.S.

Treasurer:

J. F. THORPE, C.B.E., D.Sc., F.R.S.

Secretaries:

T. SLATER PRICE, O.B.E., D.Sc., Ph.D., F.R.S.
C. S. GIBSON, O.B.E., M.A., M.Sc.

Foreign Secretary:

F. G. DONNAN, C.B.E., M.A., Ph.D., F.R.S.

Ordinary Members of Council:

H. BASSETT, D.Sc., Ph.D.
D. R. BOYD, D.Sc., Ph.D.
O. L. BRADY, D.Sc., B.A.
A. E. DUNSTAN, D.Sc.
F. A. FREETH, O.B.E., D.Sc., F.R.S.
F. W. GAMBLE.
W. N. HAWORTH, D.Sc.
C. K. INGOLD, D.Sc., F.R.S.
J. KENYON, D.Sc.
B. LAMBERT, M.A.
H. MCCOMBIE, D.S.O., M.C., D.Sc.
G. W. MONIER-WILLIAMS, O.B.E., M.C., Ph.D.
T. S. MOORE, M.A., B.Sc.
B. D. PORRITT, M.Sc.
F. L. PYMAN, D.Sc., Ph.D., F.R.S.
J. REILLY, M.A., D.Sc.
G. STUBBS, C.B.E.
F. J. WILSON, D.Sc., Ph.D.

Assistant Secretary:

S. E. CARR.

Librarian:

F. W. CLIFFORD.

BURLINGTON HOUSE, LONDON, W. 1

Telephone—GERRARD 6322.

LONDON: GURNEY AND JACKSON

33, PATERNOSTER ROW, E.C. 4

PRINTED IN GREAT BRITAIN BY RICHARD CLAY & SONS, LTD.,
BUNGAY, SUFFOLK.

Committee of Publication:

Chairman: N. V. Sidgwick, M.A., Sc.D., F.R.S.

H. B. Baker, C.B.E., D.Sc., F.R.S.
E. C. C. Baly, C.B.E., F.R.S.
H. Bassett, D.Sc., Ph.D.
O. L. Brady, D.Sc.
A. W. Crossley, C.M.G., C.B.E., F.R.S.
F. G. Donnan, C.B.E., M.A., F.R.S.
H. W. Dudley, O.B.E., M Sc., Ph.D.
U. R. Evans, M.A.
J. J. Fox, O.B.E., D.Sc.
C. S. Gibson, O.B.E., M.A.
A. J. Greenaway, F.I.C.
I. M. Heilbron, D.S.O., D.Sc.
T. A. Henry, D.Sc.
C. K. Ingold, D.Sc., F.R.S.
H. McCombie, D.S.O., M.C., D.Sc.
J. I. O. Masson, M.B.E., D.Sc.
W. H. Mills, Sc.D., F.R.S.
T. S. Moore, M.A., B.Sc.
G. T. Morgan, O.B.E., D.Sc., F.R.S.
J. R. Partington, M.B.E. D.Sc.
J. C. Philip, O.B.E., D.Sc., F.R.S.
R. H. Pickard, D.Sc., F.R.S.
T. S. Price, O.B.E., D.Sc., F.R.S.
F. L. Pyman, D.Sc., F.R.S.
J. F. Thorpe, C.B.E., D.Sc., F.R.S.
W. P. Wynne, D.Sc., F.R.S.

Editor:
Clarence Smith, D.Sc.

Indexer:
Margaret Le Pla, B.Sc.

INFORMATION FOR CANDIDATES FOR FELLOWSHIP

The Chemical Society, founded in 1841 and first granted a Royal Charter in 1848, now numbers some 4,000 Fellows. Each Fellow is entitled to receive one copy of the Journal and of such other publications of the Society as the Council may determine, to use the Library, either directly or through the post, and to take part in the meetings of the Society. Experimental work is assisted by grants from the Research Fund. Fellows are also allowed certain privileges by kindred societies.

The publications include the *Journal*, containing papers communicated to the Society, the *Abstracts*, covering the current literature in pure Chemistry, the *Indexes*, and the *Annual Reports* on the progress of Chemistry.

The *Library* contains 28,424 volumes, among which there are 293 current journals, covering applied as well as pure chemistry.

The *Meetings*, including those devoted to special lectures, number about 18 annually. Fellows resident outside London may read before British Local Sections of the Society of Chemical Industry papers intended for subsequent publication in the Journal of the Chemical Society.

The annual subscription is £3. Those desiring to become Fellows of the Society should apply for further information to the Secretaries, Burlington House, London, W. 1.

CONTENTS

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

PAGE

CCLVII.—Researches on Residual Affinity and Co-ordination. Part XXIV. Heats of Chelation of Dithiolated Metallic Halides. By GILBERT T. MORGAN, SYDNEY RAYMOND CARTER, and WILLIAM FINNEMORE HARRISON 1917

CCLVIII.—The Rotatory Dispersion of Derivatives of Tartaric Acid. Part II. Acetyl Derivatives. By PERCY CORLETT AUSTIN and JAMES RITCHIE PARK . 1926

CCLIX.—The Chemistry of Petroleum. Part II. The Action of Sodium Hypochlorite on Sulphur Compounds of the Types found in Petroleum Distillates. By STANLEY FRANCIS BIRCH and WOODFORD STANLEY GOWAN PLUCKNETT NORRIS 1934

CCLX.—The Action of Formic Acid on certain Sesquiterpenes. By JOHN MONTEATH ROBERTSON, CARL ALOYSIUS KERR, and GEORGE GERALD HENDERSON . 1944

CCLXI.—Cryoscopic Measurements with Benzene. By EDWARD RICHARD JONES and CHARLES R. BURY . 1947

CCLXII.—The Condensed Ternary System Phenol–Water–Salicylic Acid. By CHARLES REYNOLDS BAILEY . 1951

CCLXIII.—Carboxycamphoranilic Acids. By MAHAN SINGH and RAM SINGH 1966

CCLXIV.—A Synthesis of Datiscetin. By JAN KALFF and ROBERT ROBINSON 1968

CCLXV.—The Synthesis of certain 2-Styrylchromonol Derivatives. By ROBERT ROBINSON and JUNZO SHINODA . 1973

CCLXVI.—Synthetical Experiments in the *iso*Flavone Group. Part I. By WILSON BAKER and ROBERT ROBINSON 1981

CCLXVII.—Oxidation Products of Oleic Acid. Part II. Degradation of Dihydroxystearic Acid. By ARTHUR LAPWORTH and EDWARD NEVILLE MOTTRAM . . 1987

CCLXVIII.—The Effect of Ultra-violet Light on Dried Hydrogen and Oxygen. By HERBERT BRERETON BAKER and MARGARET CARLTON 1990

CCLXIX.—Imino-aryl Ethers. Part III. The Molecular Rearrangement of *N*-Phenylbenziminophenyl Ether. By ARTHUR WILLIAM CHAPMAN 1992

PAGE

CCLXX.—Substitution in Derivatives of Quinol Ethers. By Leon Rubenstein 1998

CCLXXI.—The Relative Rates of Conversion of Phenoxyphenyldichloroarsine and its Chloro-derivatives into Chlorophenoxarsines. By Elwyn Roberts and Eustace Ebenezer Turner 2004

CCLXXII.—2-Amino-4 : 5-dimethylglyoxaline. By [the late] Richard Burtles and Frank Lee Pyman . 2012

CCLXXIII.—A Synthesis of *dl*-Dicentrine. By Robert Downs Haworth, William Henry Perkin, jun., and John Rankin 2018

CCLXXIV.—Aminobenzthiazoles. Part I. 1-Anilinobenzthiazole and its Tolyl Homologues. By Robert Fergus Hunter 2023

CCLXXV.—The Amino-4-pyridones. By William Haughton Crowe 2028

CCLXXVI.—Researches on Residual Affinity and Co-ordination. Part XXV. A Quadridentate Group Contributing Four Associating Units to Metallic Complexes. By Gilbert T. Morgan and J. D. Main Smith . 2030

CCLXXVII.—The Synthesis and Reactions of 1-Anilino-*cyclo*pentane-1-carboxylic Acid. By Sydney Glenn Preston Plant and John Ernest Facer . . 2037

CCLXXVIII.—The Action of Nitrogen Dioxide on Anthracene Derivatives. By Edward de Barry Barnett 2040

CCLXXIX.—The Constitution of Indian Kamala. Part I. By Sikhibhushan Dutt 2044

CCLXXX.—The Decomposition of Carbon Monoxide in the Corona due to Alternating Electric Fields. Part I. By Miguel Crespi and Robert Winstanley Lunt . 2052

CCLXXXI.—Anode Phenomena in the Electrolysis of Potassium Ethyl Malonate. By John Braithwaite Robertson 2057

CCLXXXII.—The Reaction of Bromine with Aliphatic Acids. Catalytic Effect of Acyl Halides. By Herbert Ben Watson 2067

CCLXXXIII.—Homologues of 2 : 2′-Diquinolyl. By Edward John Venn Conolly 2083

CCLXXXIV.—The Thermal Decomposition of Ozone. By Robert Owen Griffith and Andrew McKeown . 2086

CCLXXXV.—The Dissociation Pressures of Hydrated Double Selenates. By John Ferguson . . . 2096

PAGE

CCLXXXVI.—Researches on Chromammines. Part II. Hydroxopentamminochromic Salts and Electrical Conductivities of Chromammines. By HERBERT JOSEPH SEYMOUR KING 2100

CCLXXXVII.—Electrometric Studies of the Precipitation of Hydroxides. Part I. Precipitation of Magnesium, Manganous, Ferrous, Cobalt, Nickel, and Thorium Hydroxides by Use of the Hydrogen Electrode. By HUBERT THOMAS STANLEY BRITTON 2110

CCLXXXVIII.—Electrometric Studies of the Precipitation of Hydroxides. Part II. The Precipitation of the Hydroxides of Zinc, Chromium, Beryllium, Aluminium, Bivalent Tin, and Zirconium by Use of the Hydrogen Electrode, and their Alleged Amphoteric Nature. By HUBERT THOMAS STANLEY BRITTON 2120

CCLXXXIX.—Electrometric Studies of the Precipitation of Hydroxides. Part III. Precipitation in the Cerite Group of Rare Earths and of Yttrium Hydroxide by Use of the Hydrogen Electrode. By HUBERT THOMAS STANLEY BRITTON 2142

CCXC.—Electrometric Studies of the Precipitation of Hydroxides. Part IV. Precipitation of Mercuric, Cadmium, Lead, Silver, Cupric, Uranic, and Ferric Hydroxides by Use of the Oxygen Electrode. By HUBERT THOMAS STANLEY BRITTON 2148

CCXCI.—The Interaction of Ethyl Acetoacetate and *o*-Hydroxydistyryl Ketones. Part II. By ISIDOR MORRIS HEILBRON, THOMAS ALFRED FORSTER, and ABRAHAM BRUCE WHITWORTH 2159

CCXCII.—Chemical Reactivity and Conjugation. Part II. The Reactivity of the 2-Methyl Group in the 4-Quinazolone Series. By ISIDOR MORRIS HEILBRON, FRANCIS NOEL KITCHEN, EDWARD BURDON PARKES, and GEORGE DONALD SUTTON 2167

NOTES.—Preparation of the Phenylcarbamyl Derivatives of Nitrophenols. By OSCAR L. BRADY and JACK HARRIS 2175

d-Mannitol from *Gardenia turgida*. By MARTIN ONSLOW FORSTER and KESHAVIAH ASWATH NARAIN RAO . 2176

INDEX OF AUTHORS' NAMES

Austin, P. C., and J. R. Park, 1926.
Bailey, C. R., 1951.
Baker, H. B., and (Miss) M. Carlton, 1990.
Baker, W., and R. Robinson, 1981.
Barnett, E. de B., 2040.
Birch, S. F., and W. S. G. P. Norris, 1934.
Brady, O. L., and J. Harris, 2175.
Britton, H. T. S., 2110, 2120, 2142, 2148.
Burtles, R., and F. L. Pyman, 2012.
Bury, C. R. See E. R. Jones.
Carlton, (Miss) M. See H. B. Baker.
Carter, S. R. See G. T. Morgan.
Chapman, A. W., 1992.
Conolly, E. J. V., 2083.
Crespi, M., and R. W. Lunt, 2052.
Crowe, W. H., 2028.
Dutt, S., 2044.
Facer, J. E. See S. G. P. Plant.
Ferguson, J., 2096.
Forster, M. O., and K. A. N. Rao, 2176.
Forster, T. A. See I. M. Heilbron.
Griffith, R. O., and A. McKeown, 2086.
Harris, J. See O. L. Brady.
Harrison, W. F. See G. T. Morgan.
Haworth, R. D., W. H. Perkin, jun., and J. Rankin, 2018.
Heilbron, I. M., T. A. Forster, and A. B. Whitworth, 2159.
Heilbron, I. M., F. N. Kitchen, E. B. Parkes, and G. D. Sutton, 2167.
Henderson, G. G. See J. M. Robertson.
Hunter, R. F., 2023.
Jones, E. R., and C. R. Bury, 1947.
Kalff, J., and R. Robinson, 1968.
Kerr, C. A. See J. M. Robertson.
King, H. J. S., 2100.
Kitchen, F. N. See I. M. Heilbron.
Lapworth, A., and E. N. Mottram, 1987.
Lunt, R. W. See M. Crespi.
McKeown, A. See R. O. Griffith.
Morgan, G. T., S. R. Carter, and W. F. Harrison, 1917.
Morgan, G. T., and J. D. M. Smith, 2030.
Mottram, E. N. See A. Lapworth.
Norris, W. S. G. P. See S. F. Birch.
Park, J. R. See P. C. Austin.
Parkes, E. B. See I. M. Heilbron.
Perkin, W. H., jun. See R. D. Haworth.
Plant, S. G. P., and J. E. Facer, 2037.
Pyman, F. L. See R. Burtles.
Rankin, J. See R. D. Haworth.
Rao, K. A. N. See M. O. Forster.
Roberts, E., and E. E. Turner, 2004.
Robertson, J. B., 2057.
Robertson, J. M., C. A. Kerr, and G. G. Henderson, 1944.
Robinson, R., and J. Shinoda, 1973.
Robinson, R. See also W. Baker and J. Kalff.
Rubenstein, L., 1998.
Shinoda, J. See R. Robinson.
Singh, M., and R. Singh, 1966.
Singh, R. See M. Singh.
Smith, J. D. M. See G. T. Morgan.
Sutton, G. D. See I. M. Heilbron.
Turner, E. E. See E. Roberts.
Watson, H. B., 2067.
Whitworth, A. B. See I. M. Heilbron.

ERRATA.

Vol. 127 (1925).

Page	Line	
936	17*	*for* "Grafton" *read* "Albemarle."
1750	7	*for* "(IX)" *read* "(X)."
,,	8	*add* "$CH_2{=}C{<}^{CO_2Et}_{CO_2Et}$ (X.)"
,,	12	*add* "The correct arrangement is (IX)."

* From bottom.

curve is nearly coincident with the one obtained by the hydrogen electrode, and the malonic acid curve lies closer to the true curve. The oxalic curve, however, is less satisfactory.

In conclusion, it seems that, provided the substances being titrated are not oxidising agents, the second method of calibration leads to the more satisfactory results; when oxidising agents are involved, as, for example, chromic acid, the first method is probably more satisfactory.

Summary.

(1) Oxalic, malonic, succinic, and tartaric acids and dextrose have been titrated electrometrically at 18°. The four acids produce in the course of their neutralisation hydrogen-ion concentrations which extend over the whole acid zone, and therefore partly neutralised solutions may be used for reference purposes in colorimetric determinations of p_H.

(2) The dissociation constant of dextrose as a monobasic acid has been found.

(3) Formulæ have been derived for the calculation of the dissociation constants of dibasic acids from the hydrogen electrode titration curves.

(4) The formulæ derived by Auerbach and Smolczyk have been shown to give less accurate results.

(5) Auerbach and Smolczyk's identity, $K_1K_2 = h^2$, where h is the hydrion concentration at the mid-point of the titration curve of a dibasic acid, has been shown to be erroneous.

(6) Attempts have been made to use the oxygen electrode for the purpose of indicating hydrion concentrations in titrations.

The author desires to take this opportunity to thank the Department of Scientific and Industrial Research for a personal grant, and also Prof. J. C. Philip, F.R.S., for facilities for carrying out this work.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [*Received, May 26th*, 1925.]

CCLVII.—*Researches on Residual Affinity and Co-ordination. Part XXIV. Heats of Chelation of Dithiolated Metallic Halides.*

By GILBERT T. MORGAN, SYDNEY RAYMOND CARTER, and WILLIAM FINNEMORE HARRISON.

WHEN present in organic thioethers, bivalent sulphur exhibits residual affinity to a remarkable extent so that dialkyl sulphides

combine additively with many metallic halides, giving rise to thiolated co-ordination compounds such as $2Me_2S,SnCl_4$ (Werner and Pfeiffer, *Z. anorg. Chem.*, 1898, **17**, 101), Me_2S,CdI_2 (Werner, *ibid.*, 1897, **15**, 14), $[2Me_2S,PtCl_2]$ and $[Pt,4Me_2S]PtCl_4$ (Tschugaev and Subbotin, *Ber.*, 1910, **43**, 1200). Increased stability is acquired by these thiolated metallic halides when the sulphur is present in a chelate group as in dimethyldithiolethylene, $CH_3{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_3$, a substance which functions as two associating units giving rise by implication of the metallic atom to co-ordination complexes containing one or more five-membered rings (formulæ I, II, and III).

In a previous communication (J., 1922, **121**, 2882) attention was directed to the coincidence that metallic radicals yielding the characteristic insoluble sulphides of analytical practice also give rise to well-defined co-ordination compounds with thioethers. The selective affinity between metal and sulphur is manifested in a similar manner whether in sulphide formation or in the production of thiolated metallic salts.

Moreover, in the case of metals of variable valency, both these modes of combination between metallic radical and sulphur afford an insight into the relative stabilities of the electronic structures of the metallic atoms corresponding with these valency changes.

Copper and gold, which fall into a natural family of univalent metals, have the fundamental electronic structures of Cu^{I} = 2,224,22446,**1** and Au^{I} = 2,8,18,32,18,**1** with single valency electrons. But in their cupric and auric salts the two metals exhibit alternative electronic structures, Cu^{II} = 2,224,22445,**2** and Au^{III} = 2,8,18,32,16,**3** with two and three valency electrons respectively as displayed in cupric and auric salts. In their combinations with sulphur, there is a marked tendency to revert to the lower state of valency, that is, to change from the alternative to the fundamental electronic structure. When cupric halides combine with dimethyldithiolethylene or with other thioethers the resulting thiolated cupric halides change readily to cuprous derivatives. Similarly, the thiolated auric compounds are unstable and especially sensitive to moisture, which promotes a spontaneous change to thiolated aurous derivatives (*ibid.*, p. 2883).

In the case of mercury, thiolation promotes an exaltation of valency (*ibid.*, p. 2884) corresponding with a change from the less stable electronic structure of univalent mercury, Hg^{I} = 2,8,18,32,18,1,**1**, to the more stable electronic structure of the bivalent metal, Hg^{II} = 2,8,18,32,18,**2**, which is characteristic of its natural position among the chemical elements.

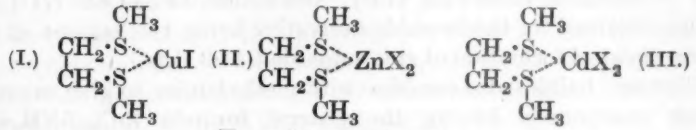
During these earlier investigations it was noticed that the formation of certain dithiolated metallic halides was accompanied by

a very appreciable rise of temperature and we have now determined the heats of chelation of fifteen of these co-ordination compounds.

With the same metallic radical it was found that the heat of combination of dithiol and metallic halides varied with the nature of the halogen, and missing members of the series were prepared in order to obtain comparative measurements.

Dimethyldithiolethylene cuprous iodide * (I), is a pale yellow substance stable in air and only slowly attacked by boiling water.

The zinc series was completed by the production of *dimethyldithiolethylene zinc chloride* and *iodide* (II), the bromide having been already described, and *dimethyldithiolethylene cadmium chloride* and *bromide* (III) were also prepared.



X = a halogen atom.

The thermal measurements described in this paper show how very vague is the former division of chemical substances into atomic and molecular compounds.

Heats of reaction do not represent exactly the free energy of change involved in building up a substance from its simpler components, and cannot, therefore, in the case of these thiolated derivatives, represent the work actually done by residual affinity, but since in many cases the free energy changes are not very different from total energy changes, a certain degree of approximation may be expected. Thus not only the free energy but also the bound energy may be assumed to have some relation to chemical structure.

The heat of chelation of cupric chloride by dimethyldithiolethylene is +14·85 Cals., whereas the heat of formation of cupric sulphide is +9·93 Cals. On the other hand, the more stable cuprous sulphide is formed with the generation of 18·26 Cals., whereas the dithiolated cuprous iodide has a heat of chelation of +5·9 Cals.

The influence of the halogen on the heat of chelation of the dithiolated metallic halides is demonstrated by a study of the complete series of mercury compounds; the data for the chloride, bromide, and iodide are in the descending order of +13·23, +11·33, and +4·83 Cals. In the case of the most exothermic of these three

* *Erratum.*—In the copper compounds each copper atom becomes associated with one molecular proportion of dithiol. The name of the cupric derivative (J., 1922, **121**, 2887) should be *dimethyldithiolethylene cupric chloride*; the prefix *bis* refers to a double molecule as in the preceding dithiolated cuprous bromide.

changes, the value exceeds appreciably that of the heat of formation of mercuric sulphide (10·75 Cals.). The three dithiolated cadmium halides give the series: chloride +12·16 Cals., bromide +11·27 Cals., and iodide +9·96 Cals., these values being all lower than the heat of formation of cadmium sulphide (34·36 Cals). It is of interest to compare the heats of chelation of this dithiolated series with the heats of co-ordination of the cadmium halides with ammonia; the latter values are as follow: $CdCl_2,2NH_3$, 37·24 Cals.; $CdBr_2,2NH_3$, 35·2 Cals.; $CdI_2,2NH_3$, 29·6 Cals. (Tassily, *Ann. Chim. Phys.*, 1899, **17**, 38).

A discrepancy was observed in the case of the dimethyldithiolethylene zinc halides, where the values were chloride, 13·21 Cals. (87°); bromide, 15·35 Cals. (79°); and iodide, 14·23 Cals. (71°), the value obtained for the bromide derivative being the highest of the three (heat of formation of zinc sulphide+41·3 Cals.).

The zinc halides also combine with methylamine to give co-ordination compounds having the general formula $ZnX_2,5NH_2{\cdot}CH_3$ (Ephraim and Linn, *Ber.*, 1913, **46**, 3742), and for these the heats of co-ordination are chloride, 12·79, bromide, 12·48, and iodide, 12·17 Cals., a diminishing series resembling the values obtained with the dithiolated cadmium and mercuric halides. However, in their combinations with ammonia (Isambert, *Compt. rend.*, 1878, **86**, 968; André, *Ann. Chim. Phys.*, 1884, **3**, 66; Tassily, *loc. cit.*) the zinc halides give the following heats of co-ordination: $ZnCl_2,4NH_3$, 68·0 Cals.; $ZnI_2,4NH_3$, 73·95 Cals.; $ZnBr_2,5NH_3$, 82·2 Cals. The ammoniated zinc bromide is anomalous both in composition and in its heat of co-ordination.

The maximum heat of chelation was observed in the case of dithiolated stannic chloride and the next highest value was noted with the corresponding bromide, the values for these two co-ordination compounds, $CH_3{\cdot}S{\cdot}C_2H_4{\cdot}S{\cdot}CH_3,SnX_2$, being 28·06 and 19·40 Cals., respectively. Stannic iodide does not yield a chelated compound, for in this combination two molecular proportions of the iodide combine with one of the dithiol, $CH_3{\cdot}S{\cdot}C_2H_4{\cdot}S{\cdot}CH_3,2SnI_4$. Nevertheless even in this case the heat of co-ordination is very considerable, being 16·58 Cals.

A heat of co-ordination of +12·0 Cals. was observed in the combination of 3 mols. of dimethyldithiolethylene with 2 mols. of bismuth iodide to form the bright scarlet complex,

$$3CH_3{\cdot}S{\cdot}C_2H_4{\cdot}S{\cdot}CH_3,2BiI_3.$$

The following table summarises the calorimetric results obtained for the heats of chelation or co-ordination, in large calories, of the fifteen dithiolated metallic halides; the heats of formation of the corresponding metallic sulphides recorded in Landolt-Börnstein

"Physikalisch-Chemische Tabellen," 1912, based on the work of Berthelot (B) and Thomsen (T), are also included.

Metal.	Dithiolated. Chloride.	Bromide.	Iodide.	Sulphide.
Copper (ic)	+14·85	—	—	+9·93 (Mean B and T)
Copper (ous)	—	—	+5·88	18·26 (T)
Zinc	13·21	+15·35	14·23	41·28 (Mean B and T)
Cadmium	12·16	11·27	9·96	34·35 (T)
Mercury	13·23	11·33	4·83	10·6 (B)
Tin	28·06	19·40	16·58	—
Bismuth	—	—	12·0	—

EXPERIMENTAL.

I. *Preparation and Purification of Dimethyldithiolethylene.*

Dimethyldithiolethylene, prepared by the action of sodium mercaptide on ethylene dibromide (Morgan and Ledbury, J., 1922, **121**, 2882), was purified through the characteristic dithiolated nickel thiocyanate, $Ni(CNS)_2,2CH_3{\cdot}S{\cdot}C_2H_4{\cdot}S{\cdot}CH_3$ (Tschugaev and Kobljamski, *Ber.*, 1908, **41**, 2222). This compound crystallised from 85% alcohol in blue needles which were dried and distilled in steam. The colourless disulphide which separated from the distillate then boiled at 182·5°/750 mm.

II. *Preparation of Dithiolated Metallic Halides.*

Dimethyldithiolethylene Zinc Chloride.—Dry chlorine was passed into a suspension of zinc dust in anhydrous ether and the disulphide was added to the filtered ethereal solution; the white dithiolated compound then separated in crystalline form, melting at 131—132° to a clear liquid. It was very unstable in a moist atmosphere and was immediately decomposed by cold water with liberation of the disulphide (Found: Zn, 25·1; Cl, 27·3; S, 24·4. $C_4H_{10}Cl_2S_2Zn$ requires Zn, 25·3; Cl, 27·45; S, 24·8%. This zinc compound was only slightly soluble in ether but very soluble in acetone; it dissolved in alcohol with decomposition.

Dimethyldithiolethylene zinc iodide was distinctly less affected by moisture than the corresponding chloride or bromide (*ibid.*, p. 2888). Zinc dust (2 g.) and iodine (6 g.) were combined in dry ether and 1 g. of the disulphide was added to the filtered solution; small, white crystals then separated, melting at 169—170° to a clear liquid (Found: Zn, 14·6; I, 57·3; S, 14·4. $C_4H_{10}I_2S_2Zn$ requires Zn, 14·8; I, 57·5; S, 14·5%). The compound was very soluble in acetone and slightly soluble in ether; it dissolved readily in methyl and ethyl alcohols with slight decomposition on boiling, but was only sparingly soluble in other solvents.

Dimethyldithiolethylene Cadmium Chloride.—On addition of the

disulphide to a solution of anhydrous cadmium chloride in dry alcohol, a white, crystalline compound separated, which was very soluble in warm alcohol and crystallised from this solvent in colourless needles; it did not melt below 285° (Found: Cd, 36·95; Cl, 23·2; S, 20·85. $C_4H_{10}Cl_2S_2Cd$ requires Cd, 36·8; Cl, 23·2; S, 21·0%). The thiolated compound was readily soluble in methyl alcohol but almost insoluble in acetone; it was slowly decomposed by cold water.

Dimethyldithiolethylene cadmium bromide, prepared in a similar manner to the preceding compound, had similar properties but did not melt below 285° (Found: Cd, 28·3; Br, 40·7; S, 16·4. $C_4H_{10}Br_2S_2Cd$ requires Cd, 28·5; Br, 40·5; S, 16·2%). The dithiolated cadmium bromide was readily soluble in acetone, ether, or methyl alcohol.

Dimethyldithiolethylene Cuprous Iodide.—A solution of copper sulphate in water was saturated with sulphur dioxide and on the addition of the organic disulphide and potassium iodide, a pale yellow substance was precipitated which was extracted with a strong solution of potassium iodide to remove any unchanged cuprous iodide. The additive compound was then washed with alcohol and dried in a vacuum desiccator. Insoluble in the ordinary organic media, it was unchanged by cold water but slowly decomposed on boiling, leaving cuprous iodide. It was very stable in air, melting and decomposing at 156°, leaving a black residue (Found: Cu, 20·1; I, 40·3; S, 20·8. $C_8H_{20}I_2S_4Cu_2$ requires Cu, 20·3; I, 40·6; S, 20·5%).

III. *Thermal Measurements.*

Description of Apparatus.—In the following calorimetric measurements the two reacting liquids were placed in separate vessels and their temperatures recorded at intervals of a minute; the one reagent was then added to the other, the temperature change being observed. A silver calorimeter of half a litre capacity was used in those cases where the metal was unattacked by the reagents. In the experiments with mercury salts a thin-walled glass calorimeter was employed. The stirrer, which consisted of two rings of sheet nickel, each perforated with eight holes and connected by nickel rods, was raised and lowered about sixty times a minute. The second liquid, contained in a tap funnel, was stirred with a small glass propeller stirrer.

The experimental methods based on the former work (Morgan and Ledbury, *loc. cit.*) were frequently modified in order to obtain reactions of a speed suitable for thermal measurements. In the case of the more stable additive compounds, the thermal data were obtained in the formation of the co-ordination compounds. For

the less stable dithiolated derivatives it was more convenient to prepare the compounds first and subsequently to determine their heats of dissociation.

Dimethyldithiolethylene cupric chloride. This compound is immediately decomposed by a large excess of water. About 2 g. of the substance were decomposed in a calorimeter and the fall in temperature was measured. The heat of dissociation was −3·77 Cals. The heat of solution of cupric chloride in water (1 : 600 water, which was the concentration employed) is given as +11·08 Cals. (Thomsen, *J. pr. Chem.*, 1875, **12**, 276). The heat of reaction of cupric chloride and the disulphide is +14·85 Cals.

Dimethyldithiolethylene cuprous iodide. Potassium iodide solution was added to a solution of copper sulphate (2·2%) and the disulphide and the resulting temperature change compared with a blank experiment in which the disulphide was absent. The difference, which gives the heat of reaction of cuprous iodide and the disulphide, was +5·88 Cals.

Dimethyldithiolethylene zinc chloride. This dithiolated chloride was decomposed with water and the heat of dissociation found to be +2·44 Cals. The heat of solution of zinc chloride (1 : 300) is given by Thomsen as +15·63 Cals. (*J. pr. Chem.*, 1875, **11**, 410). This gives the heat of reaction of zinc chloride and disulphide as +13·19 Cals.

Dimethyldithiolethylene zinc bromide (*loc. cit.*, p. 2888) was treated as in the preceding case. The heat of dissociation was −0·324 Cal. The heat of solution of zinc bromide in water is given by Thomsen as +15·03 Cals. (*J. pr. Chem.*, 1877, **16**, 328); hence the heat of reaction is +15·35 Cals.

Dimethyldithiolethylene zinc iodide. The heat of dissociation with water was −2·87 Cals., the heat of solution of zinc iodide in water (1 : 400) is +11·31 Cals. (Thomsen, *ibid.*, 1877) and hence the heat of reaction of zinc iodide and the disulphide is +14·18 Cals.

Dimethyldithiolethylene cadmium chloride. The cadmium compounds were all decomposed with 2% hydrochloric acid. The specific heat of such a solution is 0·9650 (Marignac, *Ann. Chim. Phys.*, 1876, **8**, 410). The heat of dissociation was −9·15 Cals. The heat of solution of cadmium chloride in water (1 : 400) is +3·01 Cals. (Thomsen, *ibid.*, 1875). Hence the heat of reaction of the dithiol with cadmium chloride is +12·16 Cals.

Dimethyldithiolethylene cadmium bromide. The heat of dissociation was −10·83 Cals.; the heat of solution of cadmium bromide in water (1 : 400) (Thomsen, *ibid.*, 1877) is +0·44 Cal., and hence the heat of reaction is +11·27 Cals.

Dimethyldithiolethylene cadmium iodide. The heat of dissociation was −10·92 Cals. The heat of solution of cadmium iodide in water (1 : 400) is −0·96 Cal. (Thomsen, *ibid.*, 1877). Accordingly, the heat of reaction of cadmium iodide and the disulphide is +9·96 Cals.

Dimethyldithiolethylene mercuric chloride. The heat of reaction was directly measured by the addition of the disulphide to a 3% solution of mercuric chloride in water. The specific heat of such a solution is given by Blümcke as 0·96 (*Ber.*, 1884, **17**, 555). The heat of reaction was +13·23 Cals.

Dimethyldithiolethylene mercuric bromide. A weighed amount of the disulphide was added to an alcoholic solution of mercuric bromide. The heat of solution of mercuric bromide in alcohol was ascertained to be negligible. The heat of reaction was thus found to be +11·33 Cals.

Dimethyldithiolethylene mercuric iodide. Excess of the disulphide was added to a solution of mercuric iodide in alcohol. The heat of reaction was +6·93 Cals. The heat of solution of mercuric iodide in alcohol, which was difficult to determine owing to very sparing solubility, was found to be about −2·1 Cals. Thus the heat of reaction of mercuric iodide and the disulphide is +4·83 Cals.

Trisdimethyldithiolethylene dibismuthotri-iodide. Into a solution of bismuth oxychloride in dilute hydrochloric acid about 1 g. of the disulphide was introduced. Then a solution of about one-third of the theoretical quantity of potassium iodide was added, when the characteristic red compound was formed. The heat of reaction was +35·6 Cals. and correcting for the side reactions this gives a result of +12·0 Cals. for the heat of reaction of bismuth iodide and the disulphide.

Dimethyldithiolethylene stannichloride. For the thermal measurements of the dithiolated tin compounds the copper calorimeter employed was tinned internally. A solution of the disulphide in carbon tetrachloride was run into a solution of stannic chloride in the same solvent, the co-ordination compound being insoluble in this medium. The heat of reaction was +26·98 Cals. The heat of solution of stannic chloride in the solvent was difficult to determine owing to the very hygroscopic nature of the chloride and the resulting rise in temperature. The hydration effects were minimised by leading dry carbon dioxide above the calorimeter liquid and placing fused calcium chloride between the ebonite lids; readings were taken every 15 seconds. The heat of solution (1 g. of stannic chloride to 300 g. of carbon tetrachloride) was +0·870 Cal. The heat of solution of the disulphide in the solvent was +0·232 Cal. The specific heat of carbon tetrachloride was taken as 0·2014

(Mills and MacRae, *J. physical Chem.*, 1895, **9**, 360). Correcting for the heats of solution of the reacting substances, a value of +28·06 Cals. is obtained for the heat of reaction of stannic chloride and the disulphide.

Dimethyldithiolethylene stannibromide. The heat of reaction of the bromide and disulphide, both in carbon tetrachloride solution, was +22·32 Cals. The heat of solution of stannic bromide in carbon tetrachloride was found to be —3·15 Cals. (1 g. of stannic bromide to 100 g. of carbon tetrachloride). The heat of solution of disulphide in carbon tetrachloride is +0·232 Cal.

$$C_4H_{10}S_2 + SnBr_4 \longrightarrow C_4H_{10}S_2,SnBr_4 + 19{\cdot}40 \text{ Cals.}$$

Dimethyldithiolethylene stanni-iodide. By adopting the foregoing method the reaction was not complete using the common organic solvents. Finally a solution of stannic chloride in carbon tetrachloride was added to a solution of dimethyldithiolethylene stanni-iodide in carbon tetrachloride; dimethyldithiolethylene stanni-chloride and free stannic iodide were then produced. Nearly twice the theoretical quantity of stannic chloride was necessary to complete the chemical change.

$$\underset{\text{soln.}}{C_4H_{10}S_2,2SnI_4} + \underset{\text{soln.}}{SnCl_4} \longrightarrow C_4H_{10}S_2,SnCl_4 + \underset{\text{soln.}}{2SnI_4} + 30{\cdot}30 \text{ Cals.}$$

$$\underset{\text{soln.}}{C_4H_{10}S_2} + \underset{\text{soln.}}{SnCl_4} \longrightarrow C_4H_{10}S_2,SnCl_4 + 26{\cdot}98 \text{ Cals.}$$

$$\text{Hence, } \underset{\text{soln.}}{2SnI_4} + \underset{\text{soln.}}{C_4H_{10}S_2} \longrightarrow \underset{\text{soln.}}{C_4H_{10}S_2,2SnI_4} - 3{\cdot}3 \text{ Cals.}$$

The heat of solution of stannic iodide in carbon tetrachloride (1 : 200) was found to be —3·81 Cals. The heat of solution of dimethyldithiolethylene stanni-iodide in carbon tetrachloride (1 : 200) was —27·27 Cals. The heat of solution of the disulphide in carbon tetrachloride (1 : 200) was +0·232 Cal. Hence the heat of reaction of the disulphide and stannic iodide is +16·58 Cals.

The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research and to Messrs. Brunner Mond and Company, Limited, for grants which have helped to defray the expense of this investigation.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

[*Received, June 27th,* 1925.]

CCLVIII.—*The Rotatory Dispersion of Derivatives of Tartaric Acid. Part II. Acetyl Derivatives.*

By PERCY CORLETT AUSTIN and JAMES RITCHIE PARK.

THE effect produced on the character of the rotatory dispersion of tartaric acid by bridging across various hydroxyl groups with methylene (Austin and Carpenter, J., 1924, **125**, 1939) was so remarkable that an investigation of other types of bridging became desirable. Condensation of the carboxyl groups with production of an anhydride ring is readily effected if the alcoholic groups are acetylated at the same time (Chattaway and Parkes, J., 1923, **123**, 663). Diacetyltartaric anhydride is dextrorotatory in solution in acetone or benzene and lævorotatory in alcohol or water (Anschütz and Pictet, *Ber.*, 1880, **13**, 1178; Pictet, *Arch. Sci. phys. nat.*, 1882, **7**, 82; Freundler, *Ann. Chim. Phys.*, 1895, **4**, 242), but the data recorded show considerable variations. Freundler states that whereas the rotations of dibenzoyltartaric anhydride in solution in acetone are practically independent of concentration, this is not the case with the diacetyl compound. He points out, however, that some of the solutions examined show mutarotation.* It seemed desirable, therefore, to study the compound in detail.

The Cause of the Mutarotation of Diacetyltartaric Anhydride.

We have found that if special care is taken to eliminate moisture, solutions of diacetyltartaric anhydride in acetone or ethyl acetate do not exhibit mutarotation and the strong dextrorotations are permanent. The rotations conform to the requirements of the law of "simple" rotatory dispersion (compare Austin and Carpenter, *loc. cit.*; Lowry and Cutter, this vol., p. 604). This led us to surmise that the variations in the values of the specific rotation with changes of concentration which were recorded by Freundler might also be due to the presence of moisture in the solvent. *This we have verified experimentally.* It is therefore clear that when a dry solvent is used the two principal anomalies which are characteristic of tartaric acid and of many of its derivatives, *viz.*, anomalous rotatory dispersion and sensitiveness of rotatory power to changes of concentration, disappear simultaneously.

On adding water to the dry solutions, a change of rotation soon became apparent, the rate of change increasing with the amount of water present; with one and with four molecular proportions of water, final steady values were reached after about 1½ days

* The values given by Freundler for specific rotations are obviously intended to represent molecular rotations.

and 16 days, respectively. The fact that this mutarotation is due to the hydrolysis of the anhydride ring and not to an isomeric change catalysed by the water (compare Lowry, this vol., p. 1376) was proved by isolating pure *diacetyltartaric acid* from solutions in which mutarotation was complete. The final readings were strongly lævorotatory, but the values depended on the amount of water used, as is shown in Table I.

TABLE I.

Influence of Water upon the Rotatory Power of Diacetyltartaric Acid in Acetone at 20°.

Ten g. of $C_8H_8O_7$ (anhydride) in 100 c.c. $l = 4$.

Mols. of H_2O.	a_{5780}.	a_{5461}.	a_{4359}.	Mols. of H_2O.	a_{5780}.	a_{5461}.	a_{4359}.
1	−11·23°	−13·12°	−26·43°	4	−13·10°	−15·26°	−30·31°
2	−12·18	−14·10	−28·27	5	−13·56	−15·68	−31·13
3	−12·91	−14·93	−29·29	12	−14·61	−17·00	−33·20

The cause of this increase of lævorotation with increasing amounts of water has not yet been determined. It may be due (i) to association with water molecules or (ii) to ionic dissociation of the diacetyltartaric acid. That some such influence is involved can be inferred from a study of the velocity coefficients (Table V).

The Formation of Diacetyltartaric Acid.

The results shown in Table I left us in doubt as to the true value of the rotatory power of diacetyltartaric acid until the latter substance had been isolated and identified. The purification of the acid was a somewhat troublesome process, since we were long unable to obtain any definite crystals from the solutions. Moreover, the data in reference to the properties of this acid were very meagre. Rochleder, who appears to have been the first to obtain crystals of the acid (*Sitz. Ber. Akad. Wiss. Wien*, 1859, **29**, 26), merely states that it is deliquescent; he gives neither analysis nor melting-point. W. H. Perkin, sen. (J., 1867, **20**, 138), describes the acid as a transparent, gum-like substance, whilst Colson (*Compt. rend.*, 1892, **114**, 177) obtained deliquescent crystals of a lævorotatory compound, melting at 58° and corresponding with the formula $C_8H_{10}O_8,3H_2O$. This substance we have been unable to obtain; but we have separated from solutions in benzene large, soft crystals, containing benzene of crystallisation (1½ mols.). The benzene was easily driven off by heat; the residual white powder melted at 118° and was the anhydrous acid, $C_8H_{10}O_8$. A solution of this in dry acetone was strongly lævorotatory and its rotatory dispersion was also simple. Moreover, its molecular

rotatory power was identical with that calculated from the final readings after mutarotation, when one molecular proportion of water was used. Thus, when the anhydride and water are mixed in equimolecular proportion in the presence of acetone, hydrolysis of the anhydride is complete in about 16 days and the exaltation of the lævorotation in the presence of more water must be due to some other cause.

Since the simple salts of tartaric acid have been proved to exhibit complex rotatory dispersion (Lowry and Austin, Bakerian Lecture, *Phil. Trans.*, 1922, *A*, **222**, 249), this is the first instance of simple rotatory dispersion in the tartaric acid series, which is independent of any ring formation. Even more important, however, is the fact that the anomalies have been eliminated by replacing the hydroxylic hydrogen atoms by acyl groups without bridging, whereas the substitution of alkyl groups for the carboxylic hydrogen atoms is known to be without effect.

We may therefore conclude that *the alcoholic hydroxyl groups are important, though possibly not essential factors, in the development of anomalous rotatory dispersion in tartaric acid* (compare Lowry and Austin, *Nature*, 1924, **114**, 431).

Anomalous Rotatory Dispersion caused by the Superposition of Opposite Partial Rotations.

(*a*) An interesting feature of the mutarotation of diacetyltartaric anhydride is the development of anomalous rotatory dispersion during the transition from the simple dispersion of the dextrorotatory anhydride to the simple dispersion of the lævorotatory acid. This is clearly shown in Fig. 1 and is a striking vindication of Arndtsen's hypothesis in reference to the origin of the anomalous rotatory dispersion of tartaric acid (*Ann. Chim. Phys.*, 1858, **54**, 421; Lowry and Austin, *Phil. Trans.*, *loc. cit.*; Lowry and Cutter, this vol., p. 607).

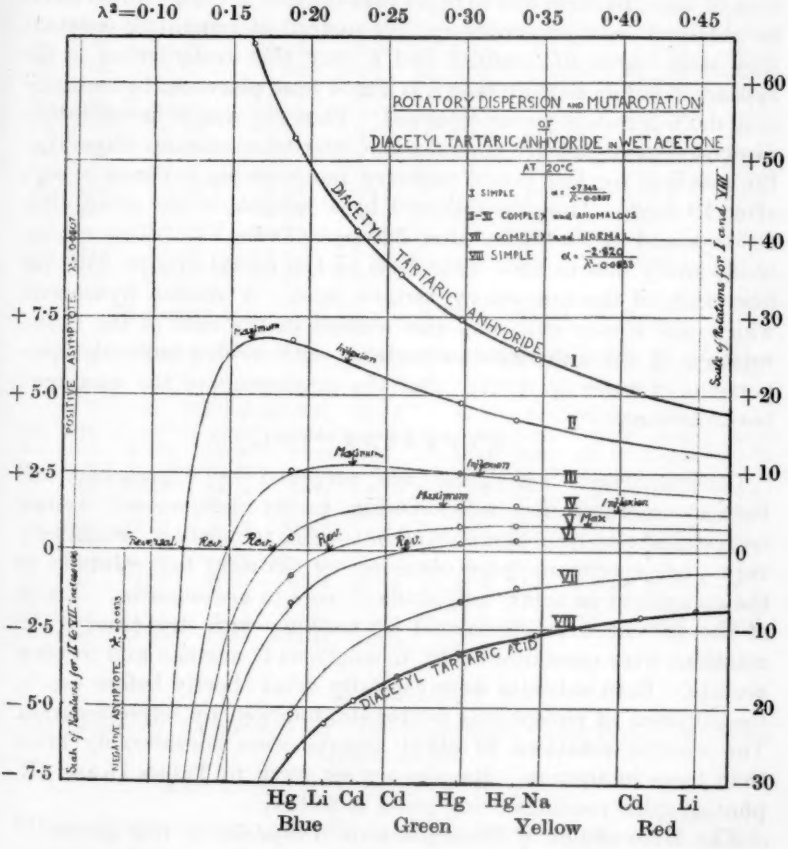
It is an essential feature of this hypothesis that the two compounds the partial rotations of which are superposed, in order to produce an anomalous dispersion, must not only be opposite in sign but of unequal dispersion. This condition is fulfilled in the present instance, since, whilst the anhydride has a dispersion-constant $\lambda^2 = 0{\cdot}0507$, the acid has a dispersion-constant $\lambda^2 = 0{\cdot}0833$, the lævo-component being the more dispersive (see Table V) just as in the case of tartaric acid and its esters (Lowry and Austin, *loc. cit.*) and of the two methylene derivatives (Austin and Carpenter, *loc. cit.*).

The figure shows the curves of simple dispersion representing the anhydride (I) and the acid (VIII) respectively together with six

intermediate curves, which are plotted on a larger vertical scale in order to show the anomalies.*

During the course of the mutarotation only the three mercury lines were read, but the form of the dispersion curves can be accurately determined by extrapolation beyond these points, since we know that we are dealing with mixtures of two known components.

FIG. 1.



It will be seen that five of the curves (II—VI) are not only *complex* but also *anomalous*, the positions of the characteristic anomalies being indicated in Table V. No. VII, although still obviously complex (since mutarotation is incomplete), is *normal*, as are also all

* The characteristic anomalies are (i) reversal of sign, λ_ρ; (ii) maximum point at λ_μ; and (iii) point of inflexion at λ_σ (Table V). In several instances the actual reversals were observed experimentally for the mercury violet, green and yellow lines in succession.

the curves (not shown in the diagram) which lie between Nos. VII and VIII. This follows necessarily from the fact that k_2 has become greater than k_1, whilst λ_2^2 is also greater than λ_1^2. Similarly, all curves which lie between I and II must be complex and anomalous.

(*b*) A change of a very similar character was observed when a solution of the anhydride in warm water was cooled to 20°. Hydrolysis of the anhydride was so rapid that the first readings which could be obtained were lævorotatory, but instead of remaining constant they soon began to diminish and a very *slow mutarotation in the opposite direction* to that shown in Fig. 1 took place until eventually only dextrorotations were observed. Thus the simple lævorotatory dispersion gave place to complex and later to anomalous dispersion, the rotation for the yellow mercury line showing reversal of sign after 19 days. This was followed by a reversal in the green after 20 days and in the violet after 32 days (Table VI). This change is obviously due to slow hydrolysis of the acetyl groups with the liberation of dextrorotatory tartaric acid. A similar hydrolysis, which was slower still, was also noticed in the case of the mutarotation of the anhydride in acetone, with twelve molecular proportions of water (p. 1927), after the attainment of the maximum lævorotations.

Experimental.

Diacetyltartaric anhydride was prepared by Chattaway and Parkes's method (*loc. cit.*). Owing to its deliquescent nature, recrystallisation from benzene did not suffice to purify it; eventually very pure specimens were obtained by allowing hot solutions of the compound in acetic anhydride to cool in a desiccator. Traces of the solvent were eliminated by washing with dry ether. The rotations were measured at 20° in solutions in acetone and in ethyl acetate. Both solvents were carefully dried shortly before use by the addition of phosphorus pentoxide, followed by refractionation. The specific rotations in ethyl acetate were considerably lower than those in acetone. Results are set forth in Tables II and III, photographic readings being given in italics.

The Mutarotation of Diacetyltartaric Anhydride in Wet Acetone.—A solution of diacetyltartaric anhydride (10 g.) in dry acetone (nearly 100 c.c.) at 20° was, after the addition of water (0·85 c.c. = 1 mol.), made up to 100 c.c. with dry solvent. The solution was transferred as rapidly as possible into a 4-dcm. tube and readings were taken at intervals measured from the moment when the water was added. Comparison of the final constant readings with those obtained from a solution of an equivalent quantity of the pure acid in dry acetone showed that the reaction was complete

TABLE II.

The Rotatory Dispersion of Diacetyltartaric Anhydride in Acetone at 20°.

(a) *First Series.* 25 G. of $C_8H_8O_7$ in 100 c.c. of solution.

Length of tube = 4 dcm. $\alpha = [\alpha]$. Simple formula $[\alpha_1] = \frac{+18{\cdot}354}{\lambda^2 - 0{\cdot}0507}$. $[M_1] = 2{\cdot}16\alpha$.

	λ.	α = [α] obs.	[α₁] calc.	[α]−[α₁].		λ.	α = [α] obs.	[α₁] calc.	[α]−[α₁].
Li	6708	+45·94°	+45·97°	−0·03°	Cu	5105	+87·45°	+87·44°	+0·01°
Cd	6438	50·49	50·45	+0·04	Cd	5086	88·17	88·25	−0·08
Zn	6364	51·92	51·80	+0·12	Zn	4811	101·50	101·54	−0·04
Li	6104	57·00	57·02	−0·02	Cd	4800	102·00	102·13	−0·13
Na	5893	61·90	61·88	+0·02	Zn	4722	106·49	106·54	−0·05
Cu	5782	64·74	64·71	+0·03	Cd	4678	108·93	109·16	−0·23
Hg	5780	64·75	64·76	−0·01	Li	4602	113·97	113·93	+0·04
Cu	5700	67·05	66·93	+0·12	Hg	4359	131·73	131·75	−0·02
Ag	5469	73·85	73·88	−0·03	*Fe*	*4157*	*150*	*150·3*	*−0·3*
Hg	5461	74·15	74·15	±	*Fe*	*4064*	*160*	*160·3*	*−0·3*
Cu	5219	82·83	82·79	+0·04	*Fe*	*4046*	*162*	*162·4*	*−0·4*
Ag	5209	83·15	83·18	−0·03	*Fe*	*3978*	*171*	*170·6*	*+0·4*
Cu	5154	85·38	85·39	−0·01					

(b) *Second Series.* 10 G. of $C_8H_8O_7$ in 100 c.c. of solution.

Length of tube = 4 dcm. $\alpha = 0{\cdot}4[\alpha]$. Simple formula $[\alpha_1] = \frac{+18{\cdot}354}{\lambda^2 - 0{\cdot}0507}$.

	λ.	α.	[α] obs.	[α₁] calc.	[α]−[α₁].		λ.	α.	[α] obs.	[α₁] calc.	[α]−[α₁].
Cd	6438	+20·20°	+50·50°	+50·45°	+0·05°	Cd	5086	35·29°	88·23°	88·25°	−0·02°
Zn	6364	20·72	51·80	51·80	±	Zn	4811	40·61	101·52	101·54	−0·02
Na	5893	24·79	61·97	61·88	+0·09	Cd	4800	40·82	102·05	102·13	−0·08
Cu	5782	25·88	64·70	64·71	−0·01	Zn	4722	42·62	106·55	106·54	+0·01
Hg	5780	25·92	64·80	64·76	+0·04	Cd	4678	43·60	109·00	109·16	−0·16
Cu	5700	26·77	66·93	66·93	±	Hg	4359	52·70	131·75	131·75	±
Ag	5469	29·52	73·80	73·88	−0·08	*Fe*	*4072*	*64*	*160*	*159·4*	*+0·6*
Hg	5461	29·66	74·15	74·15	±	*Fe*	*4046*	*65*	*162·5*	*162·4*	*+0·1*
Cu	5219	33·12	82·80	82·79	+0·01	*Fe*	*3978*	*68·2*	*170·5*	*170·6*	*−0·1*
Ag	5209	33·25	83·13	83·18	−0·05	*Fe*	*3879*	*73·5*	*183·7*	*183·9*	*−0·2*
Cu	5154	34·16	85·40	85·39	+0·01	*Fe*	*3860*	*74·8*	*187*	*186·7*	*+0·3*
Cu	5105	34·97	87·43	87·44	−0·01						

TABLE III.

The Rotatory Dispersion of Diacetyltartaric Anhydride in Ethyl Acetate at 20°.

8·250 G. of $C_8H_8O_7$ in 100 c.c. of solution.

Length of tube = 4 dcm. $\alpha = 0{\cdot}33[\alpha]$. Simple Dispersion $[\alpha_1] = \frac{+12{\cdot}177}{\lambda^2 - 0{\cdot}0570}$.

	λ.	α.	[α] obs.	[α₁] calc.	[α]−[α₁].		λ.	α.	[α] obs.	[α₁] calc.	[α]−[α₁].
Cd	6438	+11·26°	+34·12°	+34·06°	+0·06°	Cu	5105	19·79°	59·97°	59·81°	+0·16°
Zn	6364	11·64	35·27	34·99	+0·28	Cd	5086	19·98	60·54	60·38	+0·16
Na	5893	13·80	41·82	41·95	−0·13	Zn	4811	23·20	70·30	69·80	+0·50
Cu	5782	14·55	44·09	43·91	+0·18	Cd	4800	23·11	70·03	70·22	−0·19
Hg	5780	14·58	44·18	43·95	+0·23	Zn	4722	24·30	73·63	73·37	+0·26
Cu	5700	14·95	45·30	45·45	−0·15	Hg	4359	30·23	91·61	91·55	+0·06
Ag	5469	16·54	50·12	50·30	−0·18	*Fe*	*3978*	*40·0*	*121·2*	*120·3*	*+0·9*
Hg	5461	16·66	50·48	50·48	±	*Fe*	*3720*	*50·0*	*151·5*	*149·6*	*+1·9*
Cu	5219	18·66	56·54	56·54	±	*Fe*	*3609*	*55·0*	*166·7*	*166·2*	*+0·5*
Ag	5209	18·77	56·88	56·81	+0·07						

in about 16 days. Thus, since the proportion of acid to anhydride could be readily calculated at any moment, attempts were made to measure the reaction velocity coefficient. The results (Table IV) show that after a short period of induction (about 10—12 minutes) the reaction approximates more closely to the unimolecular than to the bimolecular type, but the agreement is not wholly satisfactory, since after 2 or 3 days the values of k' fall off rapidly. This fact, taken in conjunction with the gradual increase of lævorotation with increasing amounts of water (Table I), leads us to conjecture that there are probably two reactions taking place simultaneously or consecutively, *viz.* (1) opening of the anhydride ring and (2) association of anhydride or of acid with water. Previous attempts to measure the reaction velocity (Deakin and Rivett, J., 1912, **101**, 127) of this compound by conductivity measurements in aqueous solutions failed on account of the rapidity of hydration of the anhydride. We also made observations of mutarotation with larger amounts of water, but these are reserved for further investigation.

TABLE IV.

The Mutarotation of Diacetyltartaric Anhydride in Wet Acetone at 20°.

10 G. of $C_8H_8O_7$ + 0·85 g. (1 mol.) of H_2O in 100 c.c. of solution.

Length of tube 4 dcm. Values of the velocity coefficients, k' (unimolecular) and k'' (bimolecular), are calculated for $[M]_{5461}$.

Intervals (mins.).	a_{5780}.	a_{5461}.	a_{4359}.	$[M]_{5461}$.	$k' \times 10^6$.	$k'' \times 10^6$.
—	+25·92°	+29·66°	+52·70°	+160·16°	—	—
5	25·81	29·50	—	159·30	746	747
9	25·81	29·50	52·35	159·30	414	415
12	25·75	29·47	—	159·14	369	370
27	25·75	29·22	—	157·79	382	384
60	25·15	28·75	—	155·25	358	362
120	24·40	27·87	49·10	150·50	356	364
180	23·56	26·84	47·65	144·94	378	392
260	22·55	25·55	45·43	137·97	388	409
750	17·10	19·52	33·55	105·41	361	414
990	14·69	16·58	28·88	89·53	369	445
1590	9·13	10·42	16·75	56·27	376	514
2310	4·21	4·75	6·75	25·65	378	603
2700	2·38	2·50	2·50	13·50	373	644
2940	+ 1·41	+ 1·45	+ 0·45	7·83	366	658
3060	+ 0·82	+ 0·75	− 0·75	4·05	368	681
3180	+ 0·29	+ 0·23	− 1·70	+ 1·19	363	682
3690	− 1·35	− 1·64	− 5·22	− 8·86	356	739
4320	− 2·87	− 3·44	− 8·69	− 18·58	344	792
5640	− 5·38	− 6·44	−13·75	− 34·78	329	958
7200	− 7·10	− 8·38	−17·25	− 45·25	305	1114
13 days	−10·91	−12·87	−25·75	− 69·50	274	9081
∞	−11·23	−13·12	−26·43	− 70·85	—	—

The Slow Mutarotation of Diacetyltartaric Acid in Aqueous Solution.—A solution of diacetyltartaric anhydride (10 g.) in warm water was cooled and made up to 100 c.c. at 20°. The anhydride was hydro-

TABLE V.

Molecular Rotation Constants and Anomalies during the Mutarotation of Diacetyltartaric Anhydride.

$$[M] = \frac{k_1}{\lambda^2 - 0{\cdot}0507} - \frac{k_2}{\lambda^2 - 0{\cdot}0833}.$$

Dispersion.	Curve No.	Intervals in hours.	k_1.	k_2.	λ_ρ. Reversal.	λ_μ. Maximum.	λ_σ. Inflexion.
Simple	I	—	39·645	0	—	—	—
Complex and anomalous	II	38½	16·560	8·868	0·3476	0·4151	0·4733
	III	45	14·475	9·669	0·3858	0·4786	0·5565
	IV	49	13·502	10·043	0·4218	0·5363	0·6305
	V	51	12·854	10·292	0·4628	0·6159	0·7118
	VI	53	12·372	10·477	0·5134	0·6783	0·8096
Complex and normal	VII	61½	10·639	11·143	—	—	—
Simple	VIII	∞	0	15·230	—	—	—

lysed almost immediately to diacetyltartaric acid, the first reading (after an interval of 45 minutes) giving a value — 13·36° for Hg_{5461} in a 4-dcm. tube. On standing, slow mutarotation took place, the readings for the mercury yellow, green, and violet lines becoming positive after 19, 20, and 33 days respectively. Thus the rotatory dispersion became anomalous owing to the slow liberation of tartaric acid. Results are set forth in Table VI.

TABLE VI.

The Slow Mutarotation of Diacetyltartaric Acid in Aqueous Solution at 20°.

10 G. of $C_8H_8O_7$ (anhydride) in 100 c.c. of solution. $l = 4$.

Intervals.	α_{5780}.	α_{5461}.	α_{4359}.	Intervals.	α_{5780}.	α_{5461}.	α_{4359}.
45 mins.	−11·43°	−13·36°	−25·79°	31 days	+1·31°	+1·38°	−0·27°
15 hrs.	−10·29	−11·77	−23·32	33 ,,	+1·78	+1·66	+0·36
17¾ ,,	− 9·97	−11·57	−22·79	38 ,,	+1·90	+1·92	+1·07
21¼ ,,	− 9·74	−11·18	−22·02	42 ,,	+2·24	+2·34	+1·43
38¼ ,,	− 8·88	−10·03	−19·92	45 ,,	+2·48	+2·59	+1·64
62½ ,,	− 7·00	− 8·29	−17·22	48 ,,	+2·54	+2·69	+1·88
116 ,,	− 5·07	− 5·96	−11·75	56 ,,	+2·91	+3·13	+2·90
184 ,,	− 3·32	− 3·96	− 9·68	59 ,,	+3·13	+3·34	+3·05
15 days	− 0·69	− 1·00	− 4·79	62 ,,	+3·17	+3·37	+3·37
20 ,,	+ 0·18	− 0·04	− 3·03	71 ,,	+3·48	+3·62	+3·46
26 ,,	+ 0·83	+ 0·81	− 1·37				

The Preparation of Diacetyltartaric Acid, $\begin{matrix} CH_3{\cdot}CO{\cdot}O{\cdot}CH{\cdot}CO_2H \\ | \\ CH_3{\cdot}CO{\cdot}O{\cdot}CH{\cdot}CO_2H \end{matrix}$.—A solution in which mutarotation of the anhydride was complete was allowed to evaporate in a vacuum desiccator. The colourless syrup obtained (in one case only this crystallised on long standing) was dissolved in hot benzene, in which it was only slightly soluble, and the solution was allowed to remain in the desiccator. The soft, large, transparent crystals that formed slowly smelled of benzene and soon became opaque when the solvent was decanted

(Found by titration with KOH : equiv., 174·3. $C_8H_{10}O_8 + 1\frac{1}{2}C_6H_6$ requires equiv., 175·5). When the crystals were heated at 85° for 15—20 minutes and crushed, the smell of benzene was removed (Found : equiv., 116·8. $C_8H_{10}O_8$ requires equiv., 117·0). The substance, m. p. 118°, was therefore pure. A solution in dry acetone containing 10·8336 g. (equivalent to 10 g. of anhydride) in 100 c.c. was lævorotatory and the dispersion simple. The readings corresponded exactly with the final readings obtained in the mutarotation of an equivalent quantity of the anhydride in acetone containing water (1 mol.). The results are set forth in Table VII.

TABLE VII.

Rotatory Dispersion of Diacetyltartaric Acid in Acetone at 20°.

10·8336 G. of $C_8H_{10}O_8$ (equiv. to 10 g. of $C_8H_8O_7$) in 100 c.c. of solution. $l = 4$.

Simple formula $[\alpha_1] = \frac{-6{\cdot}508}{\lambda^2 - 0{\cdot}0833}$ $[M_1] = 5{\cdot}4\alpha$.

	λ.	α.	[α] obs.	[α₁] calc.	[α]—[α₁].		λ.	α.	[α] obs.	[α₁] calc.	[α]—[α₁].
Li	6708	— 7·72°	—17·81°	—17·75°	—0·06°	Cu	5105	—15·89°	—36·67°	—36·70°	+0·03°
Cd	6438	— 8·52	—19·66	—19·65	—0·01	Cd	5086	—16·07	—37·08	—37·11	+0·03
Zn	6364	— 8·74	—20·17	—20·23	+0·06	Zn	4811	—19·00	—43·84	—43·92	+0·08
Li	6104	— 9·75	—22·50	—22·50	±	Cd	4800	—19·18	—44·26	—44·24	—0·02
Na	5893	—10·65	—24·57	—24·65	+0·08	Zn	4722	—20·15	—46·50	—46·50	+0·09
Cu	5782	—11·21	—25·87	—25·92	+0·05	Cd	4678	—20·84	—48·09	—48·02	—0·07
Hg	5780	—11·23	—25·91	—25·95	+0·04	Li	4602	—22·07	—50·93	—50·65	—0·28
Cu	5700	—11·64	—26·86	—26·93	+0·07	Hg	4359	—26·43	—60·99	—60·99	±
Ag	5469	—13·08	—30·18	—30·15	—0·03	*Fe*	*4132*	*—32·5*	*—75·0*	*—74·4*	*—0·6*
Hg	5461	—13·12	—30·28	—30·28	±	*Fe*	*4046*	*—35*	*—80·8*	*—80·9*	*+0·1*
Cu	5219	—14·89	—34·36	—34·42	+0·06	*Fe*	*3978*	*—37·5*	*—86·5*	*—86·8*	*+0·3*
Ag	5209	—14·98	—34·57	—34·61	+0·04	*Fe*	*3879*	*—42*	*—96·9*	*—96·9*	±
Cu	5154	—15·48	—35·72	—35·69	—0·03						

We are indebted to the Government Grant Committee of the Royal Society for a substantial grant for the purchase of the necessary apparatus. We are also indebted to Prof. T. M. Lowry, C.B.E., F.R.S., for his criticism of this paper.

WESTMINSTER TRAINING COLLEGE,
130 HORSEFERRY ROAD, S.W. 1. [*Received, April 30th*, 1925.]

CCLIX.—*The Chemistry of Petroleum. Part II. The Action of Sodium Hypochlorite on Sulphur Compounds of the Types found in Petroleum Distillates.*

By STANLEY FRANCIS BIRCH and WOODFORD STANLEY GOWAN PLUCKNETT NORRIS.

THE refining of petroleum distillates by the "hypochlorite process" as advocated by Dunstan and Brooks (*Ind. Eng. Chem.*, 1922, **14**, 1112), which involves the oxidation of the offensive sulphur com-

pounds by means of an alkali hypochlorite, has not only been adopted as a standard method of treating the light distillates from Persian petroleum, but is rapidly becoming more generally used throughout the petroleum industry. For this reason, and more particularly because misleading statements reflecting unfavourably upon the efficiency of this process have appeared in the technical literature, it was of obvious importance to investigate the mechanism of the oxidation. In the present paper we describe the action of sodium hypochlorite solution on petroleum solutions of representative members of the types of sulphur compounds which occur in the soda-washed distillate (see Part I, this vol., p. 898).

Observations relevant to this subject have been made by Waterman and Heimal (*J. Inst. Pet. Tech.*, 1924, **46**, 812). Under the conditions they employed, diphenyl sulphide, ethyl mercaptan, carbon disulphide, diphenylsulphone, diethylsulphone, and ethyl thiocyanate were " completely removed " from petroleum solution, whilst phenyl mercaptan, diethyl sulphide, phenylthiocarbimide, phenylthiocyanate, and diphenyl sulphoxide were " substantially removed." Organic disulphides were not examined, nor were any of the oxidation products investigated. Wood, Lowy, and Faragher (*Ind. Eng. Chem.*, 1924, **16**, 1116) state quite definitely that alkyl sulphides, alkyl disulphides, and thiophen are not attacked by sodium hypochlorite solution. They also state that mercaptans are simply converted into the disulphides, which remain dissolved in the solvent employed; that they obtained no evidence of chemical action between the aqueous reagent and free sulphur, sulphoxides, or sulphones; and that hydrogen sulphide is oxidised to free sulphur and water, whilst carbon disulphide is converted into sodium carbonate and sodium sulphate.

The discrepancies between the two sets of results have made it necessary to investigate the subject anew.

It may be stated at once that all the mercaptans, organic sulphides, and organic disulphides which we have examined are quantitatively oxidised by sodium hypochlorite, the reaction proceeding quite readily provided a suitably active solution is employed, whilst thiophen and elementary sulphur remain unattacked.

The greater the tendency of a solution of sodium hypochlorite to decompose spontaneously the greater, naturally, will be its reactivity towards oxidisable compounds. Kaufmann (*Z. angew. Chem.*, 1924, **37**, 364), who considers the active agent in hypochlorite solutions to be free hypochlorous acid, $OCl' + H_2O \rightleftharpoons HOCl + OH'$, has shown that the velocity of spontaneous decomposition of aqueous sodium hypochlorite is inversely proportional to the concentration of hydroxyl ions, and that the fraction of the

total hypochlorite ions destroyed in unit time is independent of the actual concentration of hypochlorite. Thus the reactivity of a solution of sodium hypochlorite should be increased by dilution and decreased by the addition of free alkali, conclusions which have been independently reached in studying the interaction of this reagent and various compounds of sulphur. It is for this reason that, in stating certain derivatives of sulphur to be readily oxidised by hypochlorite, we have also stated that the latter must be " suitably active."

The organic solvent used was a special fraction of petroleum, b. p. 100—175°, which had been freed from aromatic compounds by shaking with a large excess of concentrated sulphuric acid, and afterwards thoroughly washed with a solution of sodium hypochlorite ; the sulphur content was thereby reduced below 0·005%.* To the petroleum thus purified, the various sulphur compounds were added in amounts sufficient to give solutions containing from 0·6% to 0·9% S. The solutions of sodium hypochlorite were prepared by leading chlorine into an aqueous solution of pure sodium hydroxide until the free alkali had been reduced to a predetermined amount; greater alkali content could then be obtained by adding solid sodium hydroxide, without appreciably altering the amount of available chlorine. The latter was determined by adding acetic acid and potassium iodide and titrating the liberated iodine. For the estimation of free alkali, the hypochlorite was first decomposed by boiling with hydrogen peroxide; the cooled liquid was then titrated with hydrochloric acid, with methyl-orange as indicator, and, the quantity of sodium carbonate being quite small, the result calculated as sodium hydroxide (*vide infra*, p. 1942).

It was usual to shake 25 c.c. of the analysed reagent with 25 c.c. of the standard solution of sulphur compound in a bottle closed by means of a cork covered with tin-foil. A mechanical shaker was used, the speed being maintained constant throughout this research. After a period of shaking previously decided upon, the petroleum layer and the aqueous liquid were separated, and analysed.

Organic Sulphides.

Since no complication arises from the formation of acidic oxidation products, it is convenient to consider first the interaction of aqueous

* All estimations of sulphur in petroleum were carried out by means of the lamp method.

We wish here to thank Miss G. E. Hickes and Mr. D. Carter, of the Analytical Department, for carrying out the numerous estimations which this research has entailed.

sodium hypochlorite and a petroleum solution of an organic sulphide. The latter is converted quantitatively into the corresponding sulphone. Not even traces of any intermediate compound (*i.e.*, a sulphoxide) could be isolated, nor does hypochlorite appear to exert any further action on sulphones; in fact, the available chlorine used up generally corresponds very closely with four atoms per atom of sulphur oxidised. The reagent does not become appreciably less alkaline during this reaction.

Kahlbaum's diethyl, di-*n*-propyl, di*iso*butyl, and di*iso*amyl sulphides were employed without further purification. In the case of diethyl sulphide, at the conclusion of the reaction, the aqueous liquid was evaporated and the residue extracted with chloroform; the diethylsulphone, m. p. 70°, obtained from the extract in 75% yield, was identified by comparison with a genuine specimen. The higher sulphones, which are more soluble in petroleum than in water, were prepared in yields of over 70% by shaking the corresponding sulphides with aqueous sodium hypochlorite alone; the resulting oils were taken up in chloroform, and after drying over calcium chloride, the solvent was removed, and the residue distilled. Di*iso*butylsulphone and di*iso*amylsulphone have b. p. 263° and 296° respectively (both with slight decomposition) (Beckmann, *J. pr. Chem.*, 1878, **17**, 448, gives b. p. 265° and 295° respectively.)

The effect of alkalinity upon the rate of oxidation of the sulphides was tested by means of eight solutions of sodium hypochlorite which contained 8·42% of available chlorine, but in which the alkalinity (calculated as sodium hydroxide) varied from 0·22% to 6·64%. Solutions of diethyl, di-*n*-propyl, di*iso*butyl, and di*iso*amyl sulphides were employed, having sulphur contents of, respectively, 0·736, 0·864, 0·912 and 0·875%. Preliminary experiments led us to adopt, for the times of shaking, 15, 30, 120, and 240 minutes, respectively. The results are summarised in Table I.

TABLE I.

Available chlorine in reagent = 8·42%.

Free alkali	Diethyl sulphide.		Di-*n*-propyl sulphide.		Di*iso*butyl sulphide.		Di*iso*amyl sulphide.	
%.	*n*.	*x*.	*n*.	*x*.	*n*.	*x*.	*n*.	*x*.
0·22	4·08	Nil	4·17	0·04	3·81	0·58	3·94	0·86
0·37	4·26	,,	4·28	0·04	3·64	0·56	3·53	0·82
0·54	4·18	,,	4·27	—	3·37	0·78	2·68	0·81
0·91	4·24	,,	4·16	0·05	2·33	0·62	1·87	0·83
1·48	4·14	,,	3·91	0·09	1·68	0·56	1·28	0·78
2·87	4·15	,,	3·05	0·25	0·87	0·74	0·88	0·82
4·14	4·14	,,	2·00	0·43	0·62	0·86	0·74	0·84
6·64	4·02	,,	1·08	0·72	0·45	0·85	0·84	0·84

n = atoms of available chlorine absorbed, per atom of sulphur present.
x = % sulphur in residual petroleum.

Diethyl sulphide was always completely oxidised after 15 minutes; since diethylsulphone is much more soluble in water than in petroleum, the latter was invariably free from sulphur. It was, however, possible to demonstrate the retarding effect of sodium hydroxide on the oxidation of diethyl sulphide by using a solution of hypochlorite which contained 20·4% of sodium hydroxide and 7·89% of available chlorine; after 15 minutes, only 21·1% of the sulphide had been oxidised, and even after 60 minutes' shaking still only 53·4% had been removed. The inhibiting influence of the free alkali is more noticeable in the oxidation of the higher sulphides. Thus, with di-*n*-propyl sulphide there is a gradual diminution in the extent of oxidation, a correspondingly increasing quantity of sulphur remaining in the petroleum. In the case of di*iso*butyl and di*iso*amyl sulphides, the figures for the residual sulphur in the petroleum are irregular; this has been traced to the existence of a partition of the resulting sulphones between the aqueous reagent and the organic solvent. It was usual, before proceeding to the analysis of the petroleum layer, to wash it once or twice with a small quantity of sodium hydroxide solution to remove any free hypochlorous acid; in consequence, varying quantities of the higher sulphones were dissolved from the petroleum. This has been confirmed, for by washing petroleum solutions of di*iso*butyl- and di*iso*amyl-sulphones several times with water the sulphur content of the petroleum was reduced. Any of the sulphides dealt with was rapidly oxidised by a dilute, faintly alkaline, solution of sodium hypochlorite. It is evident that even using so strongly alkaline a solution as one containing 6·64% of free alkali, the reaction between aqueous sodium hypochlorite and a dialkyl sulphide may be said to proceed quite readily by comparison with the prolonged reactions which are so common in synthetic organic chemistry; and even with a reagent containing 20% of free alkali the reaction with diethyl sulphide is still obvious and could scarcely fail to be detected. In fact (*vide supra*), this reaction offers a very convenient method for the preparation of sulphones.

Organic Disulphides.

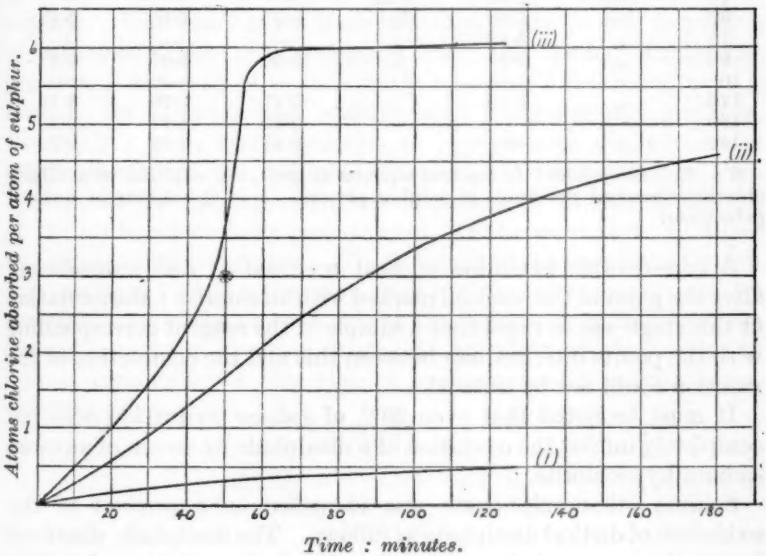
Diethyl and di*iso*propyl disulphides were quite readily freed from traces of the mercaptan or sulphide by fractional distillation. Their behaviour towards aqueous sodium hypochlorite is evidently typical of the disulphides, since parallel results were obtained in the two cases.

The primary oxidation products from diethyl disulphide, unlike the product from a sulphide, are acidic, *i.e.*, ethanesulphonic acid together with a smaller quantity of sulphuric acid; these appear as

sodium salts, and therefore the alkalinity of the aqueous phase is gradually reduced. Since the sulphonic acid (as its sodium salt) is not attacked by hypochlorite, the sulphuric acid is formed directly from the disulphide :

$$Na_2SO_4 \leftarrow H_2SO_4 \leftarrow R_2S_2 \rightarrow R{\cdot}SO_3H \rightarrow R{\cdot}SO_3Na.$$

The gradual removal of the alkali hydroxide makes it necessary, in describing the effect of alkalinity on the reaction, to distinguish two somewhat different cases. (1) The free alkali present is more than equivalent to the total possible acid products; the reagent will always remain alkaline. (2) The free alkali is less than equivalent



to the total possible acid products; if the reaction is continued long enough, the reagent will become acidic. The reaction in the first case may be described as the normal one; plotting the atoms of available chlorine absorbed, per atom of sulphur, against time, curves are obtained, of which (i), for a strongly alkaline, and (ii), for a weakly alkaline reagent, are typical. The influence of the added alkali hydroxide is very marked. If, however, the alkalinity of the reagent is so chosen that it falls into the second class, the additional complication causes the curve to assume quite a different form (iii). The initial part of the reaction takes the normal course until the acidic primary products have completely neutralised the free alkali present; at that point (*) there occurs a very rapid absorption of available chlorine until the sulphur compound is entirely removed

from the petroleum solution; the reaction then tails off and only a slow spontaneous decomposition of the residual dilute acid hypochlorite continues to take place.

TABLE II.

Diethyl disulphide. S = 0·63%. 25 C.c.

Time of shaking.	Sodium hypochlorite solution A (Cl = 5·43%; "NaOH" = 0·38%). 25 c.c.			Sodium hypochlorite solution B (Cl = 5·33%; "NaOH" = 0·73%). 25 c.c.		
Mins.	*d*.	*n*.	*x*.	*d*.	*n*.	*x*.
15	0·32	0·78	0·57	—	—	—
30	0·26	1·59	0·48	0·66	0·93	0·95
45	0·09	2·76	0·35	—	—	—
60	Nil	5·88	Nil	0·57	2·10	0·47
75	,,	5·90	,,	—	—	—
90	,,	5·91	,,	0·50	3·07	0·37
105	,,	5·98	,,	—	—	—
120	,,	6·15	,,	0·47	3·76	0·29
150	—	—	—	0·45	4·17	0·26
180	—	—	—	0·41	4·62	0·20

d = % "free alkali" in residual aqueous reagent. *n* = atoms of available chlorine absorbed per atom of sulphur present. *x* = % sulphur in residual petroleum.

A considerable evolution of heat occurred at and immediately after the point in the reaction marked with an asterisk; the oxidation at this stage was so rapid that a sample of the reagent corresponding with the points intermediate between this and the completion of the reaction could not be isolated.

It must be noted that even 20% of sodium hydroxide does not completely inhibit the oxidation of a disulphide by means of aqueous sodium hypochlorite.

Sodium ethanesulphonate was identified as a product of the oxidation of diethyl disulphide as follows. The disulphide, dissolved in petroleum, was shaken with a faintly alkaline solution of sodium hypochlorite in slight excess, until the mixture had become warm and had commenced to cool again. The aqueous liquid was warmed and treated with sulphur dioxide to decompose any residual hypochlorite and any sodium chlorate present. After adding an excess of hydrochloric acid, the excess of sulphur dioxide was expelled by boiling, and the solution neutralised, and evaporated to dryness. Sodium ethanesulphonate, mixed with sodium chloride, was extracted by means of absolute alcohol from the residue, dried at 110°. The pure salt was obtained after repeated crystallisation from absolute alcohol until it no longer contained chlorine (Found: Na, 17·4. Calc. Na, 17·5%).

A portion of the aqueous layer from the oxidation was boiled with ammonia, and hydrochloric acid and barium chloride were

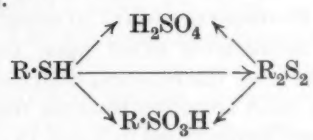
added; on boiling, a white precipitate of barium sulphate was obtained.

Mercaptans.

Ethyl mercaptan was used for these experiments; results obtained with *iso*propyl and *iso*butyl mercaptans indicated that the reactions followed the same course.

The mercaptans, before being fractionally redistilled, were washed with a small quantity of sodium hydroxide solution to remove any hydrogen sulphide.

The apparent course of the reaction between sodium hypochlorite and ethyl mercaptan depends greatly upon the alkalinity of the reagent. The first action leads simultaneously to the formation of ethanesulphonic acid, sulphuric acid, and diethyl disulphide; the last, if the reagent is sufficiently reactive, is destroyed as it is formed, the acids (as their sodium salts) being the only products. But with a more stable solution of hypochlorite a much slower decomposition of the disulphide occurs, and this substance then appears as the chief product, accompanied by smaller quantities of the acids, which have been formed, for the most part, by direct oxidation of the mercaptan. The first part of the reaction, in which the mercaptan itself takes part, does not appear to be affected by the alkalinity of the reagent, whilst the factors which influence the destruction of the resulting disulphide are those which govern the normal interaction of this type of compound with sodium hypochlorite (*vide supra*).



The proof that ethanesulphonic and sulphuric acids are formed concurrently with the disulphide is as follows: A solution of ethyl mercaptan containing 0·715% of sulphur and a solution of sodium hypochlorite containing 5·3% of available chlorine and 27·7% of sodium hydroxide being used, after 15 minutes 4·8 atoms of chlorine per atom of sulphur had been taken up, simple conversion to the disulphide requiring only one, and this figure did not appreciably increase after a further 45 minutes' agitation. This shows quite clearly that diethyl disulphide, once it is formed, is not appreciably attacked by hypochlorite having the alkalinity mentioned; this was confirmed by treating a solution of diethyl disulphide with the same reagent, when, even after 2 hours, only 0·4 atom of chlorine per atom of sulphur had been absorbed.

The influence of alkali hydroxide upon the extent of oxidation of

ethyl mercaptan during a fixed time of shaking is exhibited in Table III.

TABLE III.

Ethyl mercaptan solution : S = 0·715%.
Available chlorine = 8·42%. Time of shaking : 15 mins.

Free alkali %	0·22	0·37	0·54	0·91	1·48	2·86	4·14	6·64
Atoms Cl absorbed/atom S	7·34	7·13	6·58	6·19	5·89	5·43	5·17	5·14
% S in residual petroleum	Nil	Nil	0·03	0·11	0·12	0·14	0·15	0·19

Ethanesulphonic acid was identified in the manner described above; the sodium salt was analysed (Found : Na, 17·4%). Sulphuric acid was identified as before. Diethyl disulphide was isolated from the petroleum at the conclusion of the reaction; the yield, however, never exceeded approximately 50%.

The Influence of Sodium Carbonate and the Effect of Dilution.

Solutions of sodium hypochlorite invariably contain sodium carbonate in addition to sodium hydroxide, sodium chloride, and sodium chlorate.

During the earlier experiments, estimations were made of the actual sodium hydroxide, as well as of sodium carbonate, in the aqueous reagent. The experimental procedure thereby involved made it, however, very inconvenient to carry out a sufficient number of experiments during many of the more rapid oxidations. In seeking a more simple method for determining the alkalinity of the hypochlorite, it was therefore necessary to ascertain whether sodium carbonate has any appreciable effect upon the reactivity of the reagent. For this purpose, the reaction with diethyl disulphide was chosen, as being the most sensitive towards the influence of added alkali. The results are summarised in Table IV, in which a comparison is drawn between the course of the reaction between a standard solution of diethyl disulphide and (i) a weakly alkaline solution of sodium hypochlorite, (ii) the same solution after the addition of solid sodium carbonate.

These figures do not show any detectable increase in stability brought about by the addition of sodium carbonate. This is scarcely surprising, since no appreciable alteration is produced in the concentration of hydroxyl ions by adding sodium carbonate to a solution already containing a comparatively large quantity of sodium hydroxide.

It was, in consequence, possible to adopt quite a simple method for determining the alkalinities of a series of reagents. The object of these analyses was twofold; the decrease in the alkali present before and after a reaction gave a measure of the acid products,

TABLE IV.

Diethyl disulphide solution : S = 0·631%. 25 C.c. taken.

Time of shaking.	Sodium hypochlorite solution "A" (Cl = 5·43%; "NaOH" = 0·38%). 25 c.c.			Solution "A" plus solid sodium carbonate (Cl = 5·33%; "NaOH" = 0·38%; *Na_2CO_3 = 0·37%).			
Mins.	*d.*	*n.*	*x.*	*d.*	*n.*	*x.*	*β.*
15	0·32	0·78	0·57	0·71	0·67	0·57	2·59
30	0·26	1·59	0·48	0·64	1·49	0·51	3·24
45	0·09	2·76	0·35	0·59	2·20	0·42	7·09
60	Nil	5·88	Nil	—	—	—	—
75	,,	5·90	,,	0·20	5·71	Nil	6·88
90	,,	5·91	,,	0·20	5·73	,,	6·62
105	,,	5·98	,,	—	—	—	—
120	,,	6·15	,,	—	—	—	—

Time of shaking.	Solution "A." 25 c.c., plus 25 c.c. of water.			Solution "A." 25 c.c., plus 100 c.c. of water.		
Mins.	*d.*	*n.*	*x.*	*d.*	*n.*	*x.*
15	0·13	2·95	0·35	Nil	5·45	0·02
30	Nil	5·78	Nil	,,	5·53	Nil
45	,,	5·80	,,	—	—	—
60	,,	5·88	,,	—	—	—
75	,,	5·90	,,	—	—	—

d = % "free alkali" in residual aqueous reagent.
n = atoms of available chlorine absorbed per atom of sulphur present.
x = % sulphur in residual petroleum.
β = % of total sulphur which appears as sulphuric acid.

* Calculated as sodium hydroxide.

whilst the alkalinities of a series of reagents formed an indication of their reactivities. The solutions all contained approximately the same concentration of sodium carbonate, present as impurity in the weakly alkaline solution of sodium hypochlorite to which varying quantities of solid sodium hydroxide had been added. Since differences in alkalinity were to be compared, as distinct from the actual hydroxyl-ion concentrations, the alkalinity was estimated, after destroying the hypochlorite by means of hydrogen peroxide, by titration against hydrochloric acid with methyl-orange as indicator. Hence curves in which alkalinity is plotted as one of the co-ordinates are slightly displaced in a direction parallel to the axis of alkalinity; for the present purpose this is immaterial.

The increase in reactivity brought about by diluting a solution of sodium hypochlorite (compare p. 1936) was demonstrated by means of the reaction with diethyl disulphide. The reagent used was the same solution which had been employed for the experiments with sodium carbonate; in one series the solution was diluted to one-half, in the second to one-fifth of its original concentration. The results, which clearly indicate an increase in the velocity of reaction with

decrease in concentration of the sodium hypochlorite, are included in Table IV.

Elementary Sulphur and Hydrogen Sulphides; Thiophen.

The observation of Wood, Lowy, and Faragher (*loc. cit.*) that free sulphur is precipitated when hydrogen sulphide reacts with sodium hypochlorite, has been confirmed, but evidence of the simultaneous production of sulphuric acid has been obtained. This is not formed by further oxidation of the elementary sulphur, since the latter has been shown to be quite inert towards sodium hypochlorite.

Thiophen does not react with sodium hypochlorite.

Our thanks are due to Professor J. F. Thorpe, C.B.E., F.R.S., for his kind help and encouragement and to Dr. A. E. Dunstan and Dr. F. B. Thole for their interest in the present work.

ANGLO-PERSIAN OIL CO., LTD.,
SUNBURY-ON-THAMES. [*Received, June 13th,* 1925.]

CCLX.—*The Action of Formic Acid on certain Sesquiterpenes.*

By JOHN MONTEATH ROBERTSON, CARL ALOYSIUS KERR, and GEORGE GERALD HENDERSON.

THE experiments described below were undertaken last year as part of a larger investigation which is not yet complete, but it appears desirable to communicate the results now, in view of the interesting work carried out recently by Ruzicka and Capato (*Helv. Chim. Acta*, 1925, **8**, 259).

The action of anhydrous formic acid as a means of effecting ring closure in the sesquiterpenes is now well established. Semmler and Spornitz (*Ber.*, 1913, **46**, 4025) ascertained the transition of the aliphatic sesquiterpene from Java-citronella oil into a monocyclic isomeride by the action of concentrated formic acid. Ruzicka and Capato (*loc. cit.*) in their synthesis of bisabolene from nerolidol have now shown that the action of formic acid in the cold closes one ring in the nerolidol structure, whereas, by more prolonged action with the same reagent at a higher temperature, the closure of two rings is effected, a hexahydrocadalene being thus produced. They also observed the production of alcohols as intermediate compounds.

This reagent may also act in another way, as was shown by Wallach (*Annalen*, 1896, **289**, 337), who found that on refluxing

pulegone with anhydrous formic acid for several days, acetone and 1-methyl-3-*cyclo*hexanone resulted.

We have investigated the action of anhydrous formic acid on the dicyclic sesquiterpenes β-caryophyllene and cadinene and on the tricyclic sesquiterpene cedrene, and our results support the above conclusions with regard to the efficacy of this reagent in producing isomeric hydrocarbons and in effecting ring closure.

From β-caryophyllene we obtained the *formic* ester, $C_{16}H_{26}O_2$, of caryophyllene alcohol, together with a mixture of hydrocarbons, probably consisting of clovene and unattacked caryophyllene. Since caryophyllene alcohol is a saturated substance and on dehydration yields clovene, it is presumably tricyclic. Hence in this case the action of formic acid has effected ring closure, the sesquiterpene passing from the dicyclic caryophyllene structure to the tricyclic clovene structure.

The chief product from cadinene consisted of a hydrocarbon, or a mixture of hydrocarbons, $C_{15}H_{24}$, b. p. 118—124°/9 mm., which did not form a stable hydrochloride, together with some unchanged cadinene. On heating cadinene in an autoclave, Semmler and Jakubowicz (*Ber.*, 1914, **47**, 2252) obtained a substance, b. p. 120—130°, d 0·9025, n_D 1·50829, which they considered to be a monocyclic sesquiterpene mixed with cadinene. The product we obtained agrees closely with the above in its physical properties.

Cedrene yielded as chief product an isomeric unsaturated hydrocarbon, b. p. 114—118°/9 mm., some unchanged cedrene, and a small fraction of higher boiling point in which the presence of alcoholic compounds is suspected.

Experimental

Action of Formic Acid on β-Caryophyllene.—β-Caryophyllene was prepared by fractional distillation under diminished pressure of the commercial hydrocarbon which had stood for some time in contact with solid potassium hydroxide. The main product had b. p. 118—119°/9·7 mm., $n_D^{17°}$ 1·5009, $d_4^{17°}$ 0·9052, and gave a practically quantitative yield of the crystalline dihydrochloride of β-caryophyllene, m. p. 69°; $[\alpha]_D^{15°}$ + 67·2° in 2·5% ethyl-alcoholic solution. Caryophyllene (25 c.c.) was heated under reflux with an equal amount of formic acid for several days. A reaction set in at once, and when completed the excess of acid was neutralised with sodium carbonate, and by extraction of the mixture with ether an oil was obtained which after several fractionations yielded a colourless liquid, b. p. 141—145°/10 mm., $d_4^{17°}$ 1·22, $n_D^{20°}$ 1·4967, $[\alpha]_{5461}^{17°}$ — 10·46°. Analysis indicated that this liquid was the formic ester of caryophyllene alcohol, $C_{15}H_{25}O(CHO)$ (Found: C, 76·9; H, 10·5.

$C_{16}H_{26}O_2$ requires C, 76·8; H, 10·4%), and this was confirmed by hydrolysis of the ester, when the alcohol was obtained in crystals, which, after recrystallisation from ether–light petroleum, melted at 96°. The yield of the ester was about 35% of the caryophyllene taken. The other fractions of the distillation, b. p. 115—130°/10 mm., consisted of hydrocarbons. Heating caryophyllene in a sealed tube at 200° with anhydrous formic acid for 5 hours did not lead to an increased yield of the formic ester.

Action of Formic Acid on Cadinene.—Cadinene was prepared from the dihydrochloride, m. p. 118°, by regeneration with anhydrous sodium acetate in glacial acetic acid solution. Equal quantities of cadinene, b. p. 134—136°/11 mm., $d_4^{20°}$ 0·9189, $n_D^{20°}$ 1·5079, $[\alpha]_{5461}^{18°}$ — 125°, and 99% formic acid were heated together under reflux at 100° for 40 hours. The liquid slowly became red. After neutralisation, the products were extracted with ether and hydrolysed. The final products were distilled under diminished pressure. After several distillations two main fractions were obtained: (*a*) b. p. 118—124°/9 mm. and (*b*) b. p. 126—134°/9 mm., together with some brown resinous substances. The fraction (*a*) consisted of an unsaturated hydrocarbon, $d_4^{17°}$ 0·9086, $n_D^{14°}$ 1·5010 (Found: C, 87·3; H, 12·1. $C_{15}H_{24}$ requires C, 88·2; H, 11·85%). The fraction (*b*) consisted chiefly of unchanged cadinene.

Action of Formic Acid on Cedrene.—Cedrene, purified by distillation over sodium, b. p. 122—124°/9 mm., $d_4^{20°}$ 0·9361, $n_D^{21°}$ 1·5005, was treated with formic acid in the same way as cadinene, and the products were worked up as before. After a large number of distillations under reduced pressure, the following fractions were obtained: (*a*) b. p. 114—118°/9 mm., comprising about 50% of the product; (*b*) 118—130°/9 mm.; (*c*) 130—135°/9 mm., a small fraction. The fraction (*a*) consisted of an unsaturated hydrocarbon, $d_4^{20°}$ 0·9333, $n_D^{21°}$ 1·4988 (Found: C, 87·9; H, 11·9. $C_{15}H_{24}$ requires C, 88·2; H, 11·8%), from which no derivative could be obtained. It appears to be tricylic from its physical constants. The fraction (*b*) consisted chiefly of unattacked cedrene The fraction (*c*) appears from its analysis to contain alcoholic substances as well as hydrocarbons (Found: C, 84·8; H, 11·25%), but only a small quantity was available.

We are indebted to the Carnegie Trust for grants which enabled us to carry out this work.

UNIVERSITY OF GLASGOW. [*Received, June 13th*, 1925.]

CCLXI.—*Cryoscopic Measurements with Benzene.*

By Edward Richard Jones and Charles R. Bury.

The object of the work described in this paper was to see how far certain conclusions, reached in the study of nitrobenzene as a solvent for cryoscopy, could be applied to benzene, a far more important solvent from the point of view of ordinary laboratory practice.

First, the most important source of error is the change in water content of the solvent: this is usually overlooked with benzene, but is by no means negligible in accurate work (Sidgwick, J., 1920, **117**, 1340). The difference between the freezing point of dry and of wet benzene is 0·097° (Sidgwick, *loc. cit.*; Richards, Carver, and Schumb, *J. Amer. Chem. Soc.*, 1919, **41**, 2024). This error can be easily avoided by keeping the solvent in contact with a substance the aqueous vapour pressure of which is constant (Roberts and Bury, J., 1923, **123**, 2037).

Secondly, the usual van 't Hoff formula is strictly true only at infinite dilution; with depressions up to about 0·5° the error due to the use of this formula is less than the experimental error. At greater concentrations, however, far more accurate results may be obtained from the formula discussed by Brown and Bury (J., 1924, **125**, 2219):

$$\Delta t_u + \Delta t_w = k[n_u + Cn_v]/[n_u + (1 + C)n_v],$$

where Δt_u is the observed depression, n_u and n_v are the number of mols. of solute and solvent respectively, Δt_w and C are constants depending on the degree of moisture of the solvent, *i.e.*, on the vapour pressure of the substance with which it is in contact. These have been calculated by the method described by Brown and Bury, assuming that the freezing point of benzene is a linear function of the aqueous vapour pressure (Crowther and Puri, *Proc. Roy. Soc.*, 1924, *A*., **106**, 232). For the substances used in this research the values are:

	Aq. vap. pressure.	Δt_w.	C.
Phosphorus pentoxide, alumina ...	0·0 mm.	0	0
Na_2SO_4,0—$10H_2O$	4·40	0·063°	0·00094
Water	6·76	0·097	0·00145

With this formula it should be possible to detect combination between solute and solvent, or solvation (Washburn, "Principles of Physical Chemistry," 1915, p. 174). If every molecule of solute combines with N of solvent, the number of mols. of solute is unaltered, but the number of mols. of solvent is reduced by Nn_u: when N is 1, and the solvent is dry, the formula given reduces to that of van 't Hoff. Azobenzene, triphenylmethane, picric acid,

and trinitrotoluene, all of which separate from benzene with 1 mol. of benzene of crystallisation, have been studied to see if solvation can be detected. The existence of solid compounds is, of course, no proof that these substances form compounds with benzene in solution. It is, however, probable that the compounds of picric acid and trinitrotoluene with benzene exist in solution, since similar compounds, such as naphthalene picrate, are not entirely dissociated in inert solvents (Brown, this vol., p. 345).

EXPERIMENTAL.

The benzene used was a pure thiophen-free sample supplied by Robinson, Nelson and Co., and was further purified by the method described by Roberts and Bury (*loc. cit.*). The substances used as solutes were chosen with the idea of covering as wide a range of types of compounds as possible, and were all purified by repeated crystallisation.

The usual Beckmann method was employed. All depressions recorded are the mean of at least three closely agreeing determinations. After a number of preliminary experiments, it was decided that the loss of solvent by evaporation could not be avoided without seriously complicating the apparatus, but was negligible provided the experiment did not last more than 2½ hours.

The degree of supercooling attainable varies rather remarkably with conditions: with very pure and dry benzene it is difficult to get that small amount of supercooling which is essential to the Beckmann method; with the wet solvent, however, it is difficult to avoid a supercooling of 2°.

The freezing point of benzene has been found to be much more susceptible than that of nitrobenzene to errors due to friction and radiation, depending on the rates of stirring and the temperature of the bath. These were minimised as far as possible by maintaining a standard rate of stirring and by keeping the bath temperature 1—1·5° below the freezing point. In working with the dry solvent in the presence of phosphorus pentoxide, the usual precaution of passing dry air through the apparatus could not be used on account of the volatility of the solvent; consequently the phosphorus pentoxide soon became sticky, and the frictional effects generated by stirring made the determination of the freezing points difficult. Alumina was found to be nearly as efficient as a drying agent, and free from this disadvantage.

Conclusions.

A typical selection of the results obtained with normal solutes is given in Table I; the first column gives the weight of solute per

100 g. of solvent (W), the second the observed depression, and the third the molecular weights (M) calculated from the above formula. The solute, its molecular weight, and the degree of moisture of the solvent are given at the head. (Na_2SO_4 signifies that the solvent was partially saturated, in contact with the salt hydrate pair Na_2SO_4,0—10H_2O.) It is obvious that the calculated molecular weights are more consistent and accurate than are obtained by the usual Beckmann method, *i.e.*, by using the van 't Hoff formula, and neglecting the changing water content of the solvent.

TABLE I.

Naphthalene (128·1), dry (P_2O_5).			*p*-Dibromobenzene (235·9), dry (Al_2O_3).		
W. (g.).	Δt_u.	M.	W (g.).	Δt_u.	M.
2·504	1·005°	128·3	5·147	1·119°	236·4
3·204	1·283	128·1	9·933	2·130	236·0
5·009	1·984	128·1	11·811	2·519	235·9
5·935	2·338	128·1	13·963	2·949	236·6
6·345	2·491	128·2	16·573	3·479	236·1
7·706	3·001	128·2	19·473	4·060	235·5
10·725	4·112	128·0	21·965	4·547	235·4
Naphthalene, Na_2SO_4.			*p*-Dibromobenzene, Na_2SO_4.		
1·855	0·745	128·4	5·645	1·223	236·5
3·802	1·515	128·0	8·309	1·790	235·7
7·510	2·930	127·9	9·682	2·073	236·1
9·150	3·529	128·1	12·317	2·621	235·6
12·117	4·603	127·9	14·977	3·158	235·7
Naphthalene, saturated.			Camphor (152·2), Na_2SO_4.		
1·911	0·770	127·9	2·901	0·984	151·6
3·106	1·243	127·8	4·488	1·505	152·1
6·324	2·476	128·1	5·733	1·912	152·0
9·028	3·486	127·9	8·641	2·834	152·3
11·701	4·451	127·9	10·605	3·461	151·6
Anisole (108·1), Na_2SO_4.			Azobenzene (182·2), Na_2SO_4.		
2·515	1·192	108·1	3·806	1·071	182·5
4·060	1·907	107·9	5·702	1·594	182·2
7·976	3·649	107·8	6·865	1·907	182·5
9·171	4·161	107·9	8·432	2·331	182·2
10·257	4·629	107·6	10·473	2·866	182·5

The results obtained with the dry solvent, and quoted in this table, were used to calculate k. Assuming the theoretical molecular weights, the mean value found was 66·95, and this has been used in calculating the figures in the third column. This value corresponds to a value of 52·27 for the van 't Hoff constant, and 29·53 cals. for the latent heat of fusion of benzene. The published values for the latent heat are somewhat conflicting, and vary from 29·1 to 30·7 cals.: most direct determinations of the van 't Hoff constant are rather lower than 52·27, but it must be remembered that low values for this constant must always be obtained when working with solutions that are not infinitely dilute (Brown and Bury, *loc. cit.*).

With benzene, in which water is only very slightly soluble, little error is introduced by neglecting the water content of the solvent in calculating molecular weights, provided, of course, that it is kept constant during the experiments. If C and Δt_w are put equal to 0, as when working with the dry solvents, the calculation is considerably simplified, and the error introduced is only about 0·2%.

We have obtained no definite evidence of solvation. Azobenzene (Table I) is a perfectly normal solute. With picric acid and trinitrotoluene, the deviation that might be expected if solvation occurs is masked by a deviation in the opposite direction, possibly due to association. Triphenylmethane appears to be solvated but is, unfortunately, too insoluble for the evidence to be conclusive. The maximum depression obtainable is rather less than 0·8°, and such small depressions are liable to an experimental error of 0·5%, which is comparable with the theoretical deviation (1%) to be expected if solvation occurs. Values of k and of the van 't Hoff constant K, calculated from the experimental results with triphenylmethane, are shown in Table II. The van 't Hoff law appears to fit the

TABLE II.

Triphenylmethane (242·2), Na_2SO_4.

W. (g.).	Δt_w.	k.	K.
2·434	0·521°	67·53	52·27
2·567	0·550	67·63	52·33
2·617	0·560	67·56	52·26
2·934	0·627	67·54	52·19
3·212	0·689	67·84	52·39
3·356	0·718	67·71	52·26
3·526	0·755	67·78	52·29
	Mean	67·66	52·28
	Theory	66·95	52·27

TABLE III.

Tetrachloroethane (167·9), dry (Al_2O_3).

W. (g.).	Δt_w.	M.	k.
2·888	0·888°	167·7	67·01
4·314	1·315	168·1	66·87
5·561	1·692	167·5	67·12
8·117	2·450	166·9	67·36
12·587	3·769	164·7	68·16
14·691	4·380	163·9	68·49
17·304	5·147	162·2	69·11

results better, which indicates solvation, for the mean value of K is nearer than that of k to the values of these constants obtained with normal substances; k shows a distinct tendency to increase with the concentration whilst the variation of K is haphazard.

Substances tend to be more abnormal in benzene than in nitrobenzene. No solute which has been found normal in benzene, and which has also been studied in nitrobenzene, has proved to be abnormal in the latter solvent, but many solutes, normal in nitrobenzene, are abnormal in benzene, *e.g.*, picric acid, trinitrotoluene, methyl oxalate, α-nitronaphthalene, tetrachloroethane, and benzil. In the majority of cases these substances appear to be associated, and we hope to discuss this phenomenon fully in a later paper. Tetrachloroethane behaves in a somewhat unusual manner: it is normal in dilute solution, but the law for normal substances

breaks down at higher concentrations: as shown in Table III, the calculated molecular weights are too small at the higher concentrations.

One of us (E. R. J.) desires to acknowledge his indebtedness for a Garrod Thomas research scholarship of this College.

EDWARD DAVIES CHEMICAL LABORATORIES,
UNIVERSITY COLLEGE OF WALES,
ABERYSTWYTH.

[*Received, June 29th,* 1925.]

CCLXII.—*The Condensed Ternary System Phenol–Water–Salicylic Acid.*

By CHARLES REYNOLDS BAILEY.

TERNARY systems containing water and two organic substances have attracted workers on phase rule questions because of the varied phenomena which are to be met with. In one or more of the binary systems concerned, an upper or lower critical solution temperature frequently occurs and two liquid layers are to be found; references to many systems will be seen in Vols. II, ii, and III, ii, of Roozeboom's "Die Heterogenen Gleichgewichte" and in Tammann's work on the same subject. Difficulties in the quantitative analysis of such systems where mixtures of organic substances are involved have generally led to the restriction of their examination to the "synthetic" method; this method neglects the possible formation of mixed crystals; in the present research both analytic and synthetic methods have been applied.

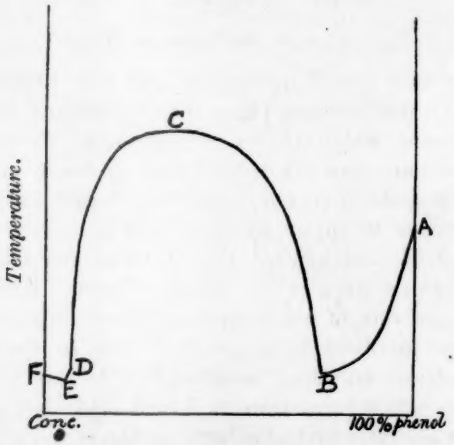
The system phenol–water–salicylic acid was chosen as it presents certain features of considerable interest and it was anticipated that by the interplay of these characteristics important solubility relations would arise. Some of the chief points are: (i) the binary system water–salicylic acid gives two liquid layers in the metastable region; (ii) the system phenol–water has two liquid layers in the stable region and the phenomenon of "melting under the liquid" occurs at an easily accessible temperature; (iii) salicylic acid has very slight solubility in water but a much higher solubility in phenol.

By use of the synthetic method it has been possible to extend the research well into the metastable region. In applying the analytic method the mixtures were stirred in a thermostat, the one or two liquid layers sucked off and, together with the moist residue, analysed as indicated below.

The Binary Systems.

(1) *Phenol–Water.*—Temperature–concentration diagrams have been given by Smits and Maarse (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 192) and by Rhodes and Markley (*J. Physical Chem.*, 1921, **25**, 527). The former workers do not give the concentrations which correspond to many of the phase changes, although the temperatures are in general agreement with those obtained by the latter workers. No trace of the stable phenol hydrate was observed in the present research and the values for certain binary and ternary mixtures are strictly metastable. The two-liquid-layer area has been explored by a large number of workers and no two determinations seem to agree, the departure from the mean being

FIG. 1.



greatest at high temperatures. In many cases this is due to the use of impure materials and in others to inaccurate use of the synthetic method. Most workers have taken as the critical saturation temperature the mean between the temperatures of clouding and clearing. If, however, the very definite temperature of sudden thickening is taken, it is possible to get readings concordant to 0·1° and agreeing with those of Timmermans (*Z. physikal. Chem.*, 1907, **58**, 129) and with the values obtained by analysis of the two liquid layers after the mixture has completely cleared in a thermostat. The difficulty does not occur to the same marked extent at lower temperatures, and it is possible to correct the concentration given by Rhodes and Markley (*loc. cit.*) for the point D (Fig. 1) where solid phenol is in equilibrium with a water-rich solution. The concentration given is 10·0% phenol at 1·7°, which is well inside the two-liquid layer area: the true concentration at this

point is 7·6% and agrees with a redetermination made by the present author by thermal analysis.

The important temperatures in the system are as follows, the letters referring to Fig. 1 :—

TABLE I.

Point.	% Phenol.	Temp.	
A	100·0	40·8°	M. p. of pure phenol
B	75·0	1·7	
C	36·5	65·3	Crit. soln. temp.
D	7·6	1·7	
E	6·5	−1·2	Eutectic
F	0·0	0·0	M. p. of ice

(2) *Salicylic Acid–Water.*—Here again many incomplete determinations are to be found in the literature; the values for the solubility of salicylic acid in water are extremely divergent: the most recent data, due to Savorro (*Atti R. Accad. Sci. Torino*, **1914**, **48**, 948) are not only above the mean of the best data available, but exhibit several breaks in the curve which do not correspond to any accompanying phase change. The values obtained in the present research (Table II) coincide with those of Walker and Wood (J., 1898, **73**, 620) up to 30°, but are slightly and uniformly larger at higher temperatures. A fresh determination of the metastable region has been made and the results differ slightly from those of Flaschner and Rankin (*Monatsh.*, 1910, **31**, 23). A careful determination of the eutectic ice–salicylic acid places this at — 0·07° and 0·103% salicylic acid.

TABLE II.

(The values are given in grams per 100 g. of solution.)

Stable.		Metastable.		
		Water	Salicylic	
% Sal.	Temp.	layer.	layer.	Temp.
0·131	10·0°	4·4	69·6	60·0°
0·184	20·0	6·5	64·6	70·0
0·261	30·0	9·8	55·9	80·0
0·395	40·0	15·0	46·0	85·0
0·592	50·0	30·0	30·0	87·0
0·864	60·0			

(3) *Phenol–Salicylic Acid.*—This system does not appear to have been previously investigated. Walden (*Z. physikal. Chem.*, **1920**, **94**, 331) found that the depression of freezing point of phenol by salicylic acid was normal. In the present case thermal analysis was resorted to; at the higher temperatures near the melting point of the acid, mixtures were sealed in glass tubes, and the temperatures of appearance and disappearance of the solid phase noted. At the lower temperatures the eutectic halts were measured

and it was found that their prolongation met the composition axis at 100% salicylic acid. Hence the system offers a simple eutectic at 5·0% salicylic acid and 38·16°. The results are given in Table III. For the mixture containing 1·5% acid the lowering of the phenol freezing point is 0·8°; if the cryoscopic constant for phenol is taken as 72·7, the molecular weight of the acid is 138·7 (calc. 138·1).

TABLE III.

No.	Wt. % of salicylic acid.	Temp.	Temp. of eutectic.	Duration of halt in minutes.
1	0·0	40·80°	—	—
2	1·64	39·95	—	—
3	3·17	39·12	38·10°	18
4	4·39	38·47	38·16	25
5	5·00	38·16	38·16	28·5
6	7·38	45·9	38·18	28
7	10·09	55·6	38·07	27·5
8	14·2	65·6	37·9	26
9	27·5	89·2	38·0	23
10	46·0	113·5	—	—
11	60·0	128·7	38·0	—
12	81·8	147·2	—	—
13	94·9	157·0	—	—
14	100·0	160·4	—	—

EXPERIMENTAL.

Materials.—(i) *Phenol.* The detached crystals marketed by the British Drug Houses seem to be a very satisfactory product, and preserve their whiteness unchanged even on long exposure to light. They were twice distilled and the end portions rejected in each case; the product obtained melted at 40·8°.

(ii) *Salicylic acid.* Both the commercial variety and the physiologically pure acid were used. The samples were recrystallised by dissolving in boiling water and pouring into cold: the process was carried out four times. This removes completely the sweet smell characterising the commercial acid, which is nevertheless of a high degree of purity nowadays. The brown colour found in specimens of the physiologically pure acid is not removed in this way. The older methods for effecting this involved distillation in steam or solution in glycerol, whereas it was found best to dissolve the acid in a hot mixture of phenol and water; on cooling, the colourless acid was precipitated and a further supply was obtained by adding water to the mixture. If the solution of the acid in hot water is allowed to cool slowly, the peculiar formation of crystalline threads may be observed (*Nature*, 1923, **112**, 10). After the last two crystallisations the m. p. was constant at 158·7°; when allowance is made for stem exposure, this figure is increased to 160·4°, a result much higher than is usually found in the literature but

agreeing with that of W. J. Bush and Co., Ltd. (*Perfumery and Essent. Oil Rec.*, 1920, **11**, 207). The value was checked by observations both on a single crystal in a melting point tube and also by cooling curves on a large bulk of the acid.

Analysis of Solutions.—Phenol was estimated by the bromide–bromate method (for details, see Redman, Weith, and Brock, *Ind. Eng. Chem.*, 1913, **5**, 389).

Salicylic acid can be directly estimated with baryta; the indicator chosen was *p*-nitrophenol with titration to a colour match. Kolthoff (*Pharm. Weekblad*, 1921, **58**, 699) has examined the bromometric method in use for phenol as applied to salicylic acid; by careful standardisation of conditions he obtained concordant results. The present author finds that with reasonable care reproducible results are obtained for one and the same concentration of acid, but if that concentration is varied the titre value does not change proportionally. Curves correlating concentration and bromide–bromate titre were constructed but found too complicated to be of use.

Phenol and salicylic acid in mixture in aqueous solution were analysed by various methods, of which the most successful were the following:

(i) By separation and subsequent determination: the phenol was extracted several times with small quantities of ether or chloroform from a solution containing a slight excess of sodium bicarbonate and the extracts were added to caustic soda solution. It was found necessary to drive off all traces of the organic solvent before bromination, as, peculiarly enough, much less bromine was taken up in its presence.

(ii) The method finally adopted was to determine first the salicylic acid alone; this can be effected by titration with baryta and *p*-nitrophenol indicator, since by keeping the phenol in low concentration it has no effect on the indicator. It was then ascertained by careful varying of the concentrations that the presence of the one substance does not affect the bromination of the other in mixtures of phenol and salicylic acid. The total bromide–bromate titre was accordingly determined for a given volume of the solution and the *same* volume of the solution was then evaporated to dryness with excess of sodium bicarbonate solution; this treatment was shown to be sufficient to drive off the phenol and leave the acid as the sodium salt, which was then brominated. The difference between the two titres gives the phenol in the mixture, since it has been shown above that with the same concentration of salicylic acid reproducible results can be obtained on bromination.

Water was determined by difference.

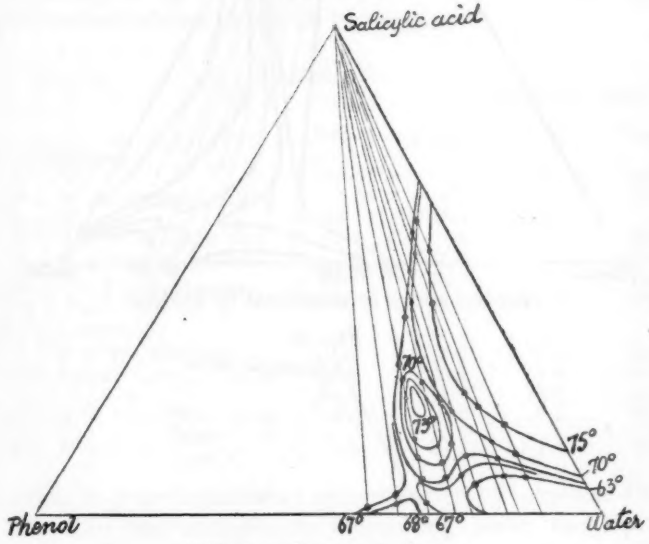
The mixtures were stirred in a thermostat for temperatures

between 20° and 70°. When equilibrium (which was approached from both sides) had been attained, the solution was sucked off through a side tube with filter into a stoppered flask and weighed, transferred to a measuring flask, and made up to a known volume. The conjugate solutions in the case of two liquid layers were allowed to settle out from the emulsion formed and sucked off; fortunately at the higher temperatures the clearing was only the matter of an hour or so; at the lower temperatures a longer period of standing was necessary. The moist residues were analysed similarly to give the solid phase.

The ternary system was also explored by the synthetic method for control purposes and to investigate the metastable region. Varying amounts of salicylic acid were added to known mixtures of phenol and water and the temperature of sudden thickening was determined; separate determinations agreed to within 0·1°. The work was carried out in sealed tubes. At the same time the temperature of the beginning of critical opalescence was determined; it was found possible to obtain reproducible readings within 0·5°. Curves were then constructed showing the relation between the above temperatures and the concentrations of salicylic acid in the particular mixture; from a given series of curves the percentages of salicylic acid present at constant temperature can be laid off: then on the usual triangular diagram the points on the phenol–water axis representing the different initial mixtures taken can be joined to the salicylic acid vertex; the percentages of acid obtained from the previous curves can be marked directly on to the triangular diagram and hence the isotherms are obtained (Figs. 2 and 3). It was found possible to complete the larger number of isotherms having metastable prolongations and so to explain the rather peculiar shape of the binodal curves. In this way two distinct series of isotherms are got and it is interesting to contrast one with the other (Figs. 2 and 3). Both temperatures from their reproducibility seem to be characteristic of the particular mixture under consideration, but it is difficult to trace any relationship between them; there are cases in which the addition of further quantities of the third component lowers the temperature of sudden thickening but actually raises the temperature of beginning of opalescence. There is apparently a " knoll " on the contour system for the critical opalescence which finds no corresponding feature on the system as determined by analysis or by the sudden thickening (the last two methods giving concordant results). Andant (*J. Phys. Radium*, 1924, **5**, 193), in an examination of the opalescence of a liquid and its vapour at the critical temperature, was able to show that the intensity and duration of the opalescence

varied with the ratio of the volume of liquid to that of vapour, passing through a maximum when the ratio was unity. In the case of binary and ternary mixtures where the upper liquid layer bears some rough analogy to the vapour phase in the unary equilibria, the correspondence would predict a condition of maximum opalescence for mixtures which are in the neighbourhood of the critical point on the particular binodal curve under consideration. This is roughly borne out by the experimental results, as will be seen on reference to Table V; in mixtures containing a large proportion of any one constituent, and hence generally resolving into

FIG. 2.



Critical opalescence isotherms.

two liquid layers with a large volume ratio, the temperatures of critical opalescence and critical thickening coincide almost exactly.

At temperatures below 20°, the system was examined by thermal analysis in a vacuum vessel; the curve which gives the displacement of the temperature at which solid phenol can exist in contact with two liquid layers on addition of the third component was obtained in that way.

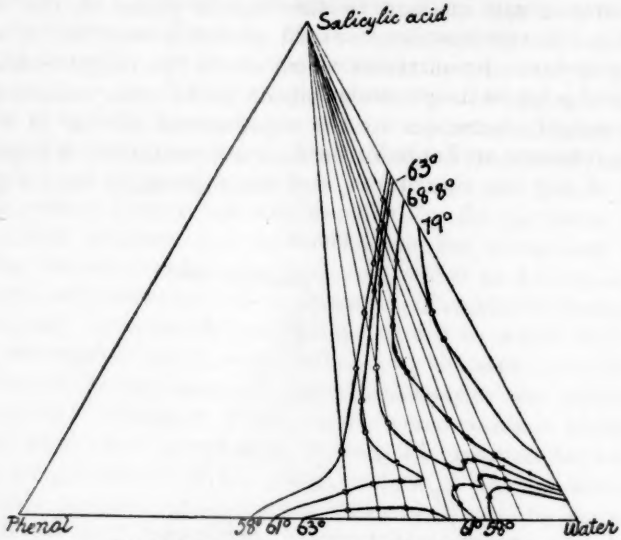
No compounds or mixed crystals were observed during the investigation.

The Isotherms.

A selection of the tabulated results will be found at the end of the paper. The two series of isotherms illustrated in Figs. 2 and 3

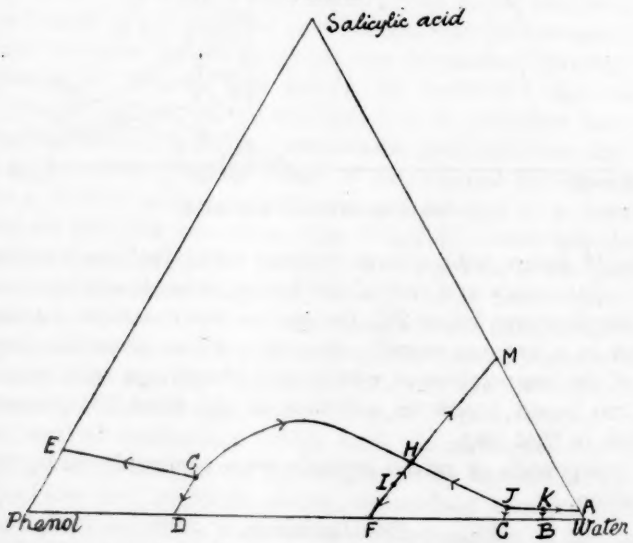
contain only the binodal curves; the inclusion of the saturation curves for solid salicylic acid would have complicated them unduly.

FIG. 3.



Binodal curves as determined by analysis.

FIG. 4.



It is expedient to consider, first, the polytherm for the system, and, secondly, the individual isotherms in order to obtain a grasp

of the many phase changes which may take place within narrow temperature limits.

The Polytherm (Fig. 4).—The actual conditions in the bottom right hand corner of the diagram have been exaggerated somewhat in order to render them apparent; the necessity for this will be readily seen on consideration of the values given below (Table IV). The arrows indicate the direction of rising temperature. To indicate the phases present the following symbols will be adopted: Solid salicylic acid S; solid phenol P; ice W; and where two coexistent liquid phases are possible: (low acid content) layer rich in phenol L_1, layer rich in water L_2; (low phenol content) layer rich in acid L_3, layer rich in water L_4. Metastable results throughout are enclosed in square brackets.

TABLE IV.

		Temp.	Percentage by weight. Phenol.	Acid.	Water.
Binary equilibria :—					
A.	S + W	−0·07°	—	0·103	99·9
B.	P + W Eutectics	−1·20	6·5	—	93·5
E.	S + W	38·16	95·0	5·0	—
C.	P + L_2 P. in equil. with	1·7	7·6	—	92·4
D.	P + L_1 two liq. layers .	1·7	75·0	—	25·0
F.	L_1 + L_2 Critical points	65·3	36·5	—	63·5
M.	[L_3 + L_4]	[87·0	—	30·0	70·0]
Ternary equilibria :—					
K.	S + P + W Eutectic ...	−1·3	6·5	0·2	93·3
I.	(See below)	61·2	20·4	7·6	72·0
H.	L_3 + L_4 + S.....	63·4	21·7	12·7	65·6
G.	S + P + L_2 Two liquid	−0·6	6·6	0·2	93·2
J.	S + P + L_1 layers, S and P.	−0·6	69·9	4·2	25·9

According to Schreinemakers's generalisation (*Z. physikal. Chem.*, 1898, **25**, 320) the temperature of melting under the liquid is depressed by the addition of a third substance when that substance is more soluble in the liquid layer which is rich in the "melting constituent." This is again confirmed: solid phenol is in equilibrium with two liquid layers at D and C; on addition of the acid the temperature and concentration of the ternary univariant phenomenon shift from B → G and C → J (from 1·7° to − 0·6°). The points K (the ternary eutectic) and J are so near to each other that the equilibria J → K are practically unrealisable. K, G, and J are system invariant points, since four phases and vapour are in equilibrium at constant pressure. F → I shows the progress of the phenol–water critical point on the addition of salicylic acid; the latter is soluble to some extent in both liquids and consequently produces a slight lowering of temperature from 65·3° to 61·2°. At I (61·2°), this binodal surface touches another binodal surface

at a second critical point; the two critical points then disappear and with lowering of temperature two binodal curves are obtained for any one temperature which have their end points not on the same base of the triangle but on S—W and P—W. The appearance of the second binodal area is due to the fact that the metastable binodal surface cuts the saturation surface of salicylic acid and has thus a stable portion. G → H and J → H give the com-

FIG. 5.

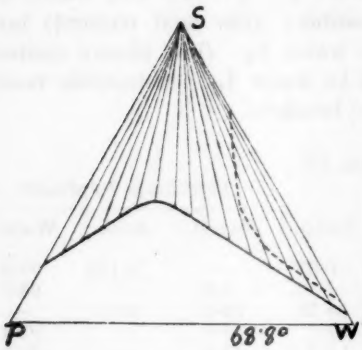
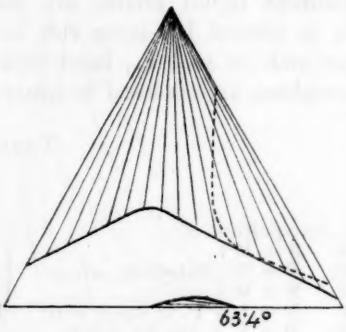


FIG. 6.



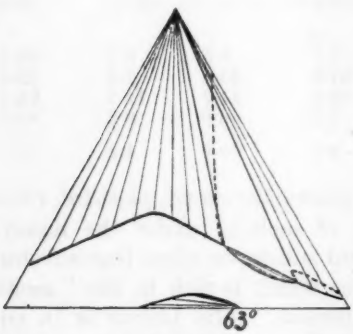


FIG. 7.

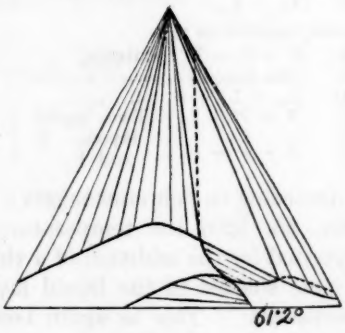


FIG. 8.

position and temperature of the univariant points where solid salicylic acid is in equilibrium with two liquid layers; again we have a curve showing the transition of the melting point under the liquid, but in this case the solid phase which melts is the third component. At H, the metastable binodal surface touches the saturation surface of salicylic acid internally at a critical point.

The Isotherms.—Certain representative isotherms have been chosen and require little elaboration. The diagrams are to some extent schematic, for it has been necessary to enlarge the con-

ditions in the water corner in order to render them visible; they represent accurately the nature of the phase changes which occur.

It will be seen that the solubility of salicylic acid is much greater in the mixed solvents than in either alone: at 68·8° the solubility of the acid in water is 1·3 g. per 100 g. of solution, in phenol 15·4 g., and at the maximum on the ternary solubility curve, 30·1 g. Below 40·8° solid phenol makes its appearance (see Fig. 11); and below 38·2° (Fig. 12) we have a three-phase area where S and P

Fig. 9.

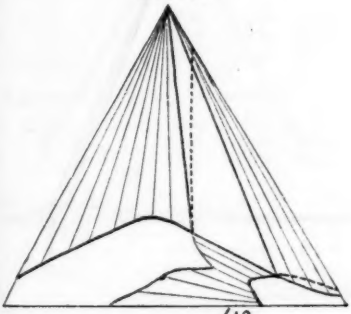
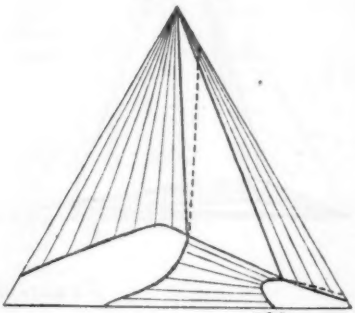


Fig. 10.



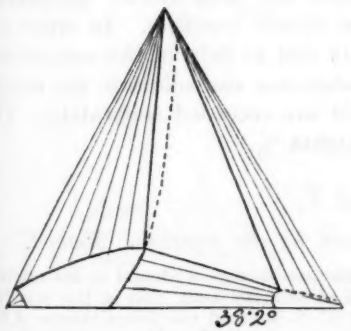


Fig. 11.

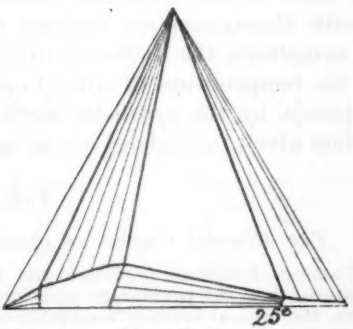


Fig. 12.

are in equilibrium with solution. From 1·7° to − 0·6° P can be in equilibrium with two liquid layers; between these two temperatures at, say, 1·0°, there are three three-phase areas (Fig. 13), the area of two coexistent liquid phases being very small. Below − 0·6° no two liquid layers are observed (Fig. 14) and finally below − 1·3° the system "dries up."

The binodal curve is a distribution curve and the distribution ratio has been determined at 25°. It has been possible to trace only one case where phenol and water have been used as the two immiscible liquids: in this case potassium iodide was found to have

more or less the same molecular weight in both solvents (Riesenfeld, *Z. physikal. Chem.*, 1902, **41**, 347). Table VIII shows that, after correction for the ionisation of the acid in the water layer (a very small effect, since $K = 0{\cdot}001$), the ratio C_w/C_p approaches constancy as the concentration of acid increases.

FIG. 13.

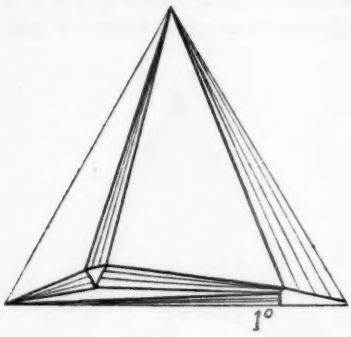
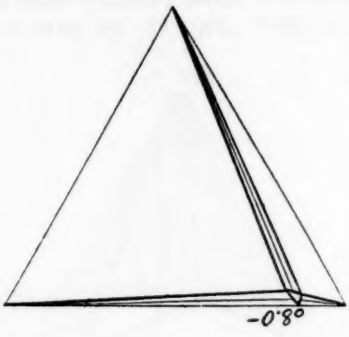


FIG. 14.



Numerical Results.

In the following tables a selection of the more important data for some of the isotherms examined has been made; metastable results throughout are enclosed in square brackets. In order not to complicate the isotherms unduly and to help in the comparison of the temperatures of critical opalescence and solution, the results obtained by the synthetic method are recorded separately. The values given throughout are in weights %.

TABLE V.

The Binodal Curves as obtained by the Synthetic Method.

Under each mixture is given : first, the percentage of phenol in the original mixture, then the percentage additions of salicylic acid, and in the last two rows, the critical solution temperature (C. S. T.) and the temperature of the beginning of critical opalescence (C. Op.).

Mixture B : 9·2% phenol.

% S.	0·0	[5·8	6·8	7·7	11·7	35·4	45·5	58·5	65·4]
C. S. T.°	32·9	58·0	61·0	63·0	68·8	79·0	79·0	68·8	58·0
C. Op.°	32·9	58·0	61·0	63·0	69·5	83·5	79·5	68·8	58·0

Mixture C : 14·6% phenol.

% S.	0·0	3·5	5·9	[6·5	7·2	9·0	15·8	53·4	61·3]
C. S. T.°	56·6	58·0	61·0	61·0	61·0	63·0	68·8	68·8	58·0
C. Op.°	56·8	59·0	62·0	62·5	63·0	65·0	71·0	69·0	58·0

Mixture K : 17·0% phenol.

% S.	0·0	6·5	8·8	[21·5	49·5	57·0	58·0]
C. S. T.°	59·7	61·0	63·0	68·8	68·0	63·0	58·0
C. Op.°	60·0	64·0	65·0	73·0	69·0	63·0	58·0

TABLE V (*continued*).

Mixture D : 20·6% phenol.

% S.	0·0	5·2	5·6	10·8	[28·0	45·3	53·3	54·7]
C. S. T.°	62·0	61·0	61·0	63·0	68·8	68·8	63·0	58·0
C. Op.°	63·2	63·5	64·0	68·0	72·0	68·8	63·0	58·0

Mixture E : 25·0% phenol.

% S.	0·0	1·3	12·6	[45·6	49·3]
C. S. T.°	63·4	63·0	63·0	63·0	58·0
C. Op°.	65·8	65·0	71·5	63·0	58·0

Mixture F : 29·9% phenol.

% S.	0·0	2·2	8·3	11·2	21·0	[39·2	42·4]
C. S. T.°	64·6	63·0	61·0	61·0	63·5	61·0	58·0
C. Op.°	67·6	66·0	69·0	70·0	73·0	61·0	58·0

Mixture G : 34·9% phenol.

% S.	0·0	2·3	8·1	16·0	[22·5	32·6]
C. S. T.°	65·3	63·0	61·0	61·0	61·0	58·0
C. Op.°	67·3	68·0	64·5	62·0	61·0	58·0

Mixture H : 41·7% phenol.

% S.	0·0	2·3	4·8	13·3	
C. S. T.°	65·0	63·0	61·0	58·0	
C. Op.°	68·3	66·0	64·0	58·0	

Mixture I : 50·8% phenol.

% S.	0·0	1·6	4·1	
C. S. T.°	62·2	61·0	58·0	
C. Op.°	64·4	63·0	59·0	

TABLE VI.

Temp. 25·0°.

No.	Phases present.	$d^{25°}_{25°}$.	Solution. P.	Solution. W.	Solution. S.	Moist solid residue. P.	Moist solid residue. W.	Moist solid residue. S.
1	S + soln.	1·0008	—	99·78	0·22	—	—	—
2	,,	1·0032	2·42	97·30	0·28	1·3	18·1	80·6
3	,,	1·0057	5·05	94·55	0·40	2·0	21·1	76·9
4	S + L_1 + L_2	1·0080	7·51	91·96	0·53	—	—	—
		1·0640	59·07	32·16	8·77			
5	S + soln.	1·0700	62·66	28·38	8·96	15·9	2·5	76·9
6	,,	1·0761	83·00	10·68	6·32	12·4	7·2	85·1
7	P + S + soln.	1·0785	90·74	4·66	4·60	—	—	—
8	P + soln.	1·0793	93·10	4·41	2·49	—	—	—
9	,,	1·0803	95·70	4·30	—	—	—	—
10	L_1 + L_2	1·0470	70·19	29·81		—	—	—
		1·0070	8·43	91·57				
11	,,	1·0500	69·28	30·21	0·51	—	—	—
		1·0072	8·35	91·61	0·04			
12	,,	1·0529	67·41	30·78	1·81	—	—	—
		1·0074	8·23	91·64	0·13			
13	,,	1·0544	65·79	31·09	3·12	—	—	—
		1·0075	8·14	91·65	0·21			
14	,,	1·0610,	60·80	31·64	7·56	—	—	—
		1·0078	7·66	91·88	0·46			

Table VII.

Temp. 30·0°.

No.	Phases present.	Solution. P.	W.	S.	Moist solid residue. P.	W.	S.
1	S + soln.	—	99·7	0·26	—	—	—
2	,,	2·6	97·0	0·40	1·4	18·2	80·4
3	,,	7·5	91·9	0·60	—	—	—
4	$L_1 + L_2 + S$	56·6	33·6	9·8	—	—	—
		8·0	91·4	0·64			
5	S + soln.	71·6	18·4	9·8	4·3	1·3	94·4
6	,,	84·9	8·0	7·1	—	—	—
7	,,	88·5	5·6	5·9	25·7	1·6	72·7
8	P + S + soln.	92·5	2·9	4·7	—	—	—
9	P + soln.	94·5	2·9	4·7	—	—	—
10	,,	97·2	2·8	—	—	—	—
11	$L_1 + L_2$	69·3	30·7		—	—	—
		9·1	90·9	—			

Temp. 44·0°.

1	S + soln.	—	99·5	0·46	—	—	—
2	,,	7·8	91·3	1·2	2·8	17·3	79·9
3	$L_1 + L_2 + S$	47·8	38·5	13·6	—	—	—
		8·9	89·7	1·4			
4	S + soln.	49·6	36·0	14·4	25·5	19·9	54·6
5	,,	56·8	27·8	15·4	12·0	6·0	82·0
6	,,	61·9	22·8	15·3	2·2	2·4	95·4
7	,,	70·9	14·8	14·3	27·0	4·3	68·7
8	,,	87·8	4·0	8·2	43·6	2·2	54·2
9	,,	82·8	7·1	10·1	48·6	4·3	47·1
10	,,	92·5	—	7·5	—	—	—
11	$L_1 + L_2$	63·8	35·5	0·72	—	—	—
		10·1	89·8	0·09			
12	,,	59·0	36·7	4·3	—	—	—
		10·4	89·2	0·44			
13	,,	52·6	38·2	9·2	—	—	—
		9·7	89·3	1·0			
14	,,	50·3	38·4	11·3	—	—	—
		9·6	89·2	1·2			
15	,,	64·2	35·8	—	—	—	—
		10·2	89·8				

Temp. 58·0°.

1	S + soln.	—	99·2	0·80	—	—	—
2	,,	7·7	89·9	2·3	1·9	31·6	66·5
3	$L_1 + L_2 + S$	33·2	49·4	17·4	—	—	—
		12·7	83·9	4·3			
4	S + soln.	48·0	29·1	22·9	—	—	—
5	,,	55·6	22·0	22·4	21·1	7·5	71·4
6	,,	73·2	10·0	16·8	—	—	—
7	,,	89·0	—	11·0	—	—	—
8	$L_1 + L_2$	44·2	49·0	6·8	—	—	—
		14·5	83·1	2·4			
9	$L_1 + L_2$	15·3	84·7	—	—	—	—
		55·6	44·4	—			
10	$L_1 + L_2$	[—	96·0	4·0]	—	—	—
		[—	29·4	70·6]			

TABLE VII (*continued*).

Temp. 61·0°.

1	$L_1 + L_2 + S$	28·1	51·9	20·0	
		13·5	80·9	5·6	
2	$L_1 + L_2$	15·9	77·5	6·6	
		28·3	59·7	12·0	
3	,,	19·3	74·7	6·0	No solid residues were determined for this and higher temperatures.
		23·0	68·5	8·5	
4	,,	19·3	75·7	5·0	
		29·0	63·0	8·0	
5	,,	18·9	81·1	—	
		52·8	47·2	—	
6	,,	[—	95·4	4·6]	
		[—	32·8	67·2]	

Temp. 63·0°.

No.	Phases present.	Solution. P.	W.	S.
1	S + soln.	—	99·0	1·0
2	,,	11·5	83·3	5·2
3	,,	14·2	78·2	7·6
4	$S + L_3 + L_4$	25·2	60·0	15·8
		14·5	77·9	8·5
5	S + soln.	34·2	45·2	20·6
6	,,	87·0	—	13·0
7	Crit. pt. $(L_1 + L_2)$	31·8	65·3	2·9
8	$L_1 + L_2$	43·0	55·1	1·9
		20·5	78·7	0·8
9	,,	23·0	77·0	—
		49·3	50·7	—
10	Crit. pt. $(L_3 + L_4)$	18·0	72·0	10·0
11	$L_3 + L_4$	16·0	75·0	9·0
		22·3	65·2	12·5
12	,,	[—	95·4	4·6]
		[—	31·4	68·6]

Temp. 68·8°.

No.	Phases present.	Solution. P.	W.	S.
1	S + soln.	—	98·7	1·3
2	,,	9·6	84·4	6·0
3	,,	19·9	63·1	17·0
4	,,	38·0	34·4	27·6
5	,,	45·9	24·0	30·1
6	,,	60·0	15·0	25·0
7	,,	84·6	—	15·4

TABLE VIII.

The Distribution of Salicylic Acid between Phenol and Water at 25·0°.

(*The numbers refer to the corresponding points in Table VI.*)

C_w (after correction for ionisation) and C_p, the concentrations in the respective solvents, are given in grams per litre.

No.	C_w.	C_p.	C_w/C_p.	No.	C_w.	C_p.	C_w/C_p.
11	0·38	5·36	0·0709	14	4·57	77·72	0·0570
12	1·27	19·07	0·0668	4	5·28	93·34	0·0565
13	2·07	32·93	0·0629				

My acknowledgments are due to Professor F. G. Donnan, F.R.S., for his kindly help and guidance; and to the Research Fund Committee of the Chemical Society for a grant which has covered the cost of materials used.

THE WILLIAM RAMSAY LABORATORIES OF PHYSICAL AND INORGANIC CHEMISTRY,
UNIVERSITY COLLEGE, LONDON. [*Received, May 27th,* 1925.]

CCLXIII.—*Carboxycamphoranilic Acids.*

By MAHAN SINGH and RAM SINGH.

TINGLE and his co-workers (*Amer. Chem. J.*, 1907, **37**, 596; **38**, 642; 1908, **39**, 1892), as a result of their researches on the intramolecular rearrangement of phthalamic acids, conclude that the change of these acids into phthalimides

$$C_6H_4<\begin{matrix}CO\cdot NH\cdot C_6H_4R\\CO_2H\end{matrix} \rightarrow C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot C_6H_4R+H_2O$$

is dependent on the following factors: (1) the nature of the group R, the stability of the acid increasing as R becomes more negative (stability: $CO_2H > NO_2 > OH >$ halogens); (2) the nature of the amine, the amine being more active, the more strongly positive it is; (3) the temperature; (4) the presence of a solvent such as ethyl alcohol.

The reactions of camphoric anhydride with *o*-, *m*-, and *p*-aminobenzoic acids have now been investigated. They proceed thus:

$$C_8H_{14}<\begin{matrix}CO\\CO\end{matrix}>O+H_2N\cdot C_6H_4\cdot CO_2H = C_8H_{14}<\begin{matrix}CO\cdot NH\cdot C_6H_4\cdot CO_2H.\\CO_2H\end{matrix}$$

The carboxycamphoranilic acids produced are very stable and have not been converted into camphorimides at various temperatures, in various solvents, or by treatment with mild dehydrating agents such as fused sodium acetate and anhydrous sodium sulphate. Hence it appears that if the imide is formed at all, it is so unstable that it is immediately hydrolysed. This may be due to the extreme negativity of the carboxyl group.

The condensation product consists of only one acid in each case; whether it is the α- or the β-camphoranilic acid (compare Singh and Biswas, J., 1924, **125**, 1895) has not been determined.

With regard to the optical rotations of the three carboxycamphoranilic acids, (1) the *o*-carboxy-compound gives negative values; (2) a regularity can be observed between the molecular rotation and the position of the carboxyl group. In all solvents, the order is $p > m > o$; (3) for a given acid in different solvents, the rotatory power diminishes in the order: methyl alcohol, ethyl alcohol, acetone, methyl ethyl ketone. The dielectric constants of these solvents are 35·4, 20·8, 21·5, and 17·8, respectively. The rotatory power, therefore, is lowest in the solvent which has the lowest dielectric constant.

EXPERIMENTAL.

Condensation of Camphoric Anhydride with Aminobenzoic Acids. General Method.—Camphoric anhydride and the aminobenzoic acid (equal mols.) are heated together with fused sodium acetate. The product is dissolved in 80% alcohol (alcohol in the case of the

m-carboxy-compound) and precipitated by the addition of water and scratching, being decolorised by charcoal and by repetition of the process if necessary.

2′-Carboxycamphoranilic acid, $CO_2H{\cdot}C_8H_{14}{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H$ (temperature of condensation, 125—130°; time, 3 hours. The yield is seriously affected by variation in temperature, being almost nil above 160°) separates in crystals containing $3H_2O$. It melts at 75—80°, then shrinks, solidifies, and finally melts at 199—200°. It is soluble in ethyl alcohol, methyl alcohol, or acetone, and sparingly soluble in benzene or chloroform (Found : C, 55·0; H, 7·1; N, 3·65; equiv., by titration with NaOH, 187·5. Found, in material heated at 75—80° for 1 hour : C, 64·4; H, 6·8. $C_{17}H_{21}O_5N,3H_2O$ requires C, 54·7; H, 7·2; N, 3·75%; equiv., dibasic, 186·5. $C_{17}H_{21}O_5N$ requires C, 63·95; H, 6·6%).

3′-Carboxycamphoranilic acid (temperature of condensation, 160°; time, 3 hours; yield nearly quantitative) is a white, amorphous powder, m. p. 249°, which is soluble in ethyl alcohol, methyl alcohol, or acetone, but insoluble in benzene, chloroform, or ether (Found : C, 63·7; H, 6·9; N, 4·5; equiv., 161. $C_{17}H_{21}O_5N$ requires C, 63·95; H, 6·6; N, 4·4%; equiv., 159·5).

4′-Carboxycamphoranilic acid (temperature of condensation, 140—145°; time, 4 hours; yield 95%) separates as a white, amorphous mass which melts at 149—150°, shrinks, re-solidifies, and finally melts at 212°. It is slightly soluble in water, readily soluble in ethyl alcohol, methyl alcohol, or acetone, but only very sparingly so in benzene, ether, or chloroform (Found : C, 60·05; H, 7·4; N, 4·2; equiv., 169·5. Found, in material heated for 1 hour at 135—145° : equiv., 160. $C_{17}H_{21}O_5N,H_2O$ requires C, 60·5; H, 6·8; N, 4·15%; equiv. 168·5. $C_{17}H_{21}O_5N$ requires equiv., 159·5).

Molecular Rotations of the Carboxycamphoranilic Acids.

Solvent.	Conc. g./25 c.c.	Temp.	α_D.	$[\alpha]_D$.	$[M]_D$.
	2′-Carboxycamphoranilic acid, $C_{17}H_{21}O_5N,3H_2O$.				
MeOH	0·0798	18°	−1·00°	−157°	−584°
EtOH	0·0974	17	−1·20	−154	−574
Me_2CO	0·1624	17	−1·92	−148	−551
MeEtCO	0·1294	17	−1·08	−104·5	−390
	3′-Carboxycamphoranilic acid, $C_{17}H_{21}O_5N$.				
MeOH	0·1309	19	+1·53	+146	+466
EtOH	0·0962	17	1·04	135	431
Me_2CO	0·1084	17	1·12	129	412
MeEtCO	0·0714	17	0·56	98	313
	4′-Carboxycamphoranilic acid, $C_{17}H_{21}O_5N,H_2O$.				
MeOH	0·0744	19	+1·52	+255	+860
EtOH	0·1155	17	1·98	214	722
Me_2CO	0·1046	17	1·76	210	709
MeEtCO	0·0820	17	1·08	165	555

The readings were taken in a 2-dcm. tube within 30 minutes of making up the solution. There was no mutarotation.

The authors desire to thank Dr. H. B. Dunnicliff for guidance and practical help during this investigation.

GOVERNMENT COLLEGE,
LAHORE, INDIA. [*Received, April 15th*, 1925.]

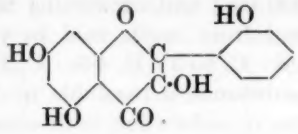
CCLXIV.—*A Synthesis of Datiscetin.*

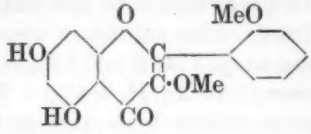
By JAN KALFF and ROBERT ROBINSON.

DATISCIN was isolated by Braconnot in 1816 (*Ann. Chim. Phys.*, **3**, 277) from the leaves of the Bastard Hemp, *Datisca cannabina*, but his largely correct description was ignored and datiscin regarded as identical with inulin until the accurate work of Stenhouse (*Ann. Ch. Pharm.*, 1855, **98**, 166; *Chem. Gaz.*, 1856, No. 318) re-established the individuality of the compound, which he isolated from the roots of the plant. Stenhouse showed that on hydrolysis with acids datiscin yields glucose and datiscetin, $C_{30}H_{10}O_{12}$ (C = 6; O = 8), which by fusion with potassium hydroxide gives salicylic acid or by boiling with dilute nitric acid is changed into nitrosalicylic acid. Roots of *Datisca* from Kew Gardens were examined by Schunck and Marchlewski (*Annalen*, 1893, **277**, 266), who concluded that datiscin is a rhamnoside. The datiscetin isolated in the course of that work had m. p. 237° and differed in some of its properties from the datiscetin of Stenhouse. Fortunately, a small specimen of the material has been preserved in the Schunck Collection housed in the Chemistry Department of this University, and we are of the opinion that it consists essentially of datiscetin mixed with galangin (see p. 1972). It seems possible that the datiscin from the Kew roots was a mixture of galangin rhamnoside and datiscetin glucoside.

Korczyński and Marchlewski (*Bull. Acad. Sci. Cracovie*, 1906, A, 95; 1907, A, 124) again isolated datiscin, from *Datisca* roots from the Punjab, and showed that it gives glucose on hydrolysis. Moreover, after removal of a methoxyl-containing substance, datiscetin, $C_{15}H_{10}O_6$, m. p. 268—269°, was obtained and characterised and this was clearly the true datiscetin of Stenhouse. From the reactions of datiscetin and the fact that it yields phloroglucinol as well as salicylic acid on fusion with potassium hydroxide, Leškiewicz and Marchlewski (*ibid.*, 1914, A, 218; *Ber.*, 1914, **47**, 1599) drew the conclusion that the substance is 3 : 5 : 7 : 2′-tetrahydroxyflavone (I). The 3 : 5 : 7-trimethyl ether of this flavonol

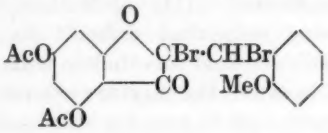
has been synthesised by Bargellini and Peratoner (*Gazzetta*, 1919, **49**, ii, 64), who employed the methods of von Kostanecki, but the derivative has not yet been related to natural datiscetin.

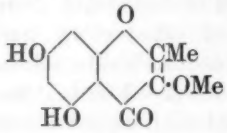
(I.) 



(II.)

The synthesis now described is an application of the method of Allan and Robinson (J., 1924, **125**, 2192) already used by the present authors (this vol., p. 181) for the syntheses of galangin monomethyl ether and myricetin. ω-Methoxyphloracetophenone (Slater and Stephen, J., 1920, **117**, 316) reacts at 180° with *o*-methoxybenzoic anhydride and sodium *o*-methoxybenzoate to give a product which yields *datiscetin* 3 : 2′-*dimethyl ether* (II) on hydrolysis. On demethylation with hydriodic acid, datiscetin (I) was obtained and we are greatly indebted to Professor Marchlewski for specimens of natural datiscetin and some of its derivatives which have enabled us to make the necessary direct comparisons.

(III.) 

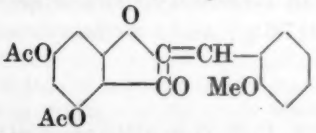


(IV.)

In some earlier experiments an attempt was made to apply the von Auwers flavonol synthesis (compare *Ber.*, 1915, **48**, 85) to the case of datiscetin. The *compound* III was obtained without difficulty, but no trace of a flavonol could be isolated from the products of its decomposition with alkaline solutions. An attempt was also made to synthesise datiscetin 3-monomethyl ether and accordingly ω-methoxyphloracetophenone was brought into reaction with *o*-acetoxybenzoic anhydride and sodium *o*-acetoxybenzoate. Curiously enough, the acetoxy-groups alone function and we found that the product was 3-*methoxy*-5 : 7-*dihydroxy*-2-*methylchromone* (IV).

EXPERIMENTAL

2-o-*Methoxybenzylidene*-4 : 6-*diacetoxycoumaranone*,



—A satisfactory yield of the methyl ether was obtained by treating salicylaldehyde with methyl sulphate (5 mols.) and aqueous sodium

hydroxide at about 40°. A mixture of *o*-methoxybenzaldehyde (4·1 g.), 4 : 6-dihydroxycoumaranone (5 g.) (Sonn, *Ber.*, 1917, **50**, 1265), and acetic anhydride (90 c.c.) was boiled for 2¼ hours. The product was added to hot water (500 c.c.) and on stirring the oil solidified. The substance crystallised from acetic acid in yellow prisms, m. p. 174° (yield 55%) (Found: C, 65·3; H, 4·5. $C_{20}H_{16}O_7$ requires C, 65·2; H, 4·4%). This substance is insoluble in dilute aqueous sodium hydroxide and gives no coloration with alcoholic ferric chloride. It is sparingly soluble in alcohol or benzene and readily soluble in chloroform. The *dibromide* (formula III) was obtained by the addition with cooling and stirring of bromine (2·4 g.) in chloroform (15 c.c.) to a solution of the methoxybenzylidenediacetoxycoumaranone (5·5 g.) in chloroform (25 c.c.). Evolution of hydrogen bromide did not occur and, after 45 minutes, the substance was precipitated by light petroleum (80 c.c.) and rapidly crystallised from much hot alcohol, separating in small, colourless prisms, m. p. 163° (decomp.) (Found: Br, 31·2, 31·1. $C_{20}H_{16}O_7Br_2$ requires Br, 30·3%). As frequently observed in similar cases, some nuclear bromination has clearly occurred.*

3 : 2′-*Dimethoxy*-5 : 7-*dihydroxyflavone* (II).—*o*-Methoxybenzoic acid of satisfactory purity being somewhat difficult to obtain, an aqueous alkaline solution of salicylic acid was shaken with methyl sulphate (2—3 mols.), the acids isolated, the mixture esterified, and washed with aqueous sodium hydroxide to remove ethyl salicylate. The neutral ester was then hydrolysed.

Comparison of the different processes available for the preparation of *o*-methoxybenzoic anhydride (Rule and Paterson, J., 1924, **125**, 2161) showed that the following is the most convenient (compare D.R.-P. 201325). A 20% solution of carbonyl chloride (1 mol.) in benzene was gradually added with careful cooling to one of the acid (2 mols.) and pyridine (1 mol.) in the same solvent. After 2 hours, the mixture was treated with crushed ice and very dilute sulphuric acid, when the precipitate dissolved. The benzene solution was then further agitated with ice and dilute aqueous sodium carbonate for ½ hour, dried, and the solvent removed by distillation in a vacuum. The residue solidified and was sufficiently pure for most purposes (yield 85%). The product obtained by heating a mixture of ω-methoxyphloracetophenone (5 g.), sodium *o*-methoxybenzoate (7·5 g.), and *o*-methoxybenzoic anhydride (19 g.)

* On prolonged contact with dry methyl alcohol the colourless dibromide changed to yellow prisms which fall to a yellow powder, m. p. 192–193°, at 50–60° [Found: OMe, 7·3. $C_{19}H_{12}O_6Br(OMe)$ requires OMe, 6·95%]. It appears, therefore, that the elements of hydrogen bromide are eliminated and that this process is not accompanied by the introduction of further methoxyl groups.

for 3 hours at 180° was hydrolysed with potassium hydroxide (8·5 g.) in aqueous or alcoholic solution. The phenol, precipitated as a viscous, brown mass by saturating the diluted solution with carbon dioxide, was again treated with aqueous potassium hydroxide on the steam-bath and after isolation as before could be crystallised from aqueous acetic acid (yield 6 g. or 75%). This product was acetylated by treatment with boiling acetic anhydride in presence of sodium acetate. The *diacetyl* derivative crystallised from methyl alcohol in colourless, flat, pointed needles, m. p. 141·5—142·5° (corr.) (Found: C, 63·1; H, 4·5. $C_{21}H_{18}O_8$ requires C, 63·3; H, 4·5%) and was hydrolysed by gently heating with aqueous potassium hydroxide. The datiscetin dimethyl ether, obtained by saturation of the solution with carbon dioxide, crystallised from alcohol in almost colourless, glistening needles, m. p. 218—219° (corr.) [Found: MeO by micro-Zeisel, 19·7. $C_{15}H_8O_4(OMe)_2$ requires MeO, 19·7%]. The yellow solution in sulphuric acid gradually acquires a weak green fluorescence and a yellow solution results when a few drops of a mineral acid are added to a suspension of the dimethyldatiscetin in acetic acid. An alcoholic solution gives a blackish-green coloration with ferric chloride. Mordant dyeing properties were not observed.

Datiscetin (I).—A mixture of 5 : 7-diacetoxy-3 : 2′-dimethoxyflavone (1 g.) and hydriodic acid (15 c.c.; *d* 1·7) was boiled for 30 minutes, and the hot solution filtered (Jena sintered glass) and allowed to cool. The dark yellow crystals of the hydriodide were collected, decomposed by very dilute sulphurous acid, and crystallised from alcohol. The m. p. was at first 260°, but by continued recrystallisation a product, m. p. 276° (corr.), was ultimately obtained in long, pale yellow needles. The specimen of natural datiscetin which was available had m. p. 270·5—271·5° (corr.) and an intimate mixture of the two specimens melted at 273—274° (corr.). The reactions and dyeing properties of the two products were identical. The tetra-acetyl derivative, prepared in the usual manner, crystallised from alcohol in large, colourless, glistening prisms, m. p. 141° (corr.) (Found: C, 60·8; H, 4·0. Calc. for $C_{23}H_{18}O_{10}$, C, 60·8; H, 4·0%). Korczyński and Marchlewski (*loc. cit.*) give 138° (uncorr.) as the m. p. of datiscetin tetra-acetate. The synthetical specimen was also benzoylated by following the method of Korczyński and Marchlewski (*loc. cit.*); the product crystallised from 90% acetic acid in star-shaped aggregates of small needles, m. p. 191—192° (corr.), and at the same temperature when mixed with a specimen prepared from natural datiscetin.

3 : 7 : 2′-*Trimethoxy*-5-*hydroxyflavone*.—Datiscetin dimethyl ether (1 mol.) was methylated by means of methyl iodide (4 mols.) and

potassium hydroxide (4 mols.) in boiling methyl-alcoholic solution for 12 hours. The product crystallised from methyl alcohol in long, colourless needles, m. p. 111—112·5° [Found : MeO, 28·1. $C_{15}H_7O_3(OMe)_3$ requires MeO, 28·3%]. This substance is sparingly soluble in cold methyl alcohol and gives a dull brownish-green coloration with ferric chloride. It is insoluble in cold aqueous sodium hydroxide and on boiling the material becomes yellow but does not dissolve.

3-*Methoxy*-5 : 7-*dihydroxy*-2-*methylchromone* (IV).—A mixture of ω-methoxyphloracetophenone (5 g.), *o*-acetoxybenzoic anhydride (D.R.-P. 201325) (23 g.) and sodium *o*-acetoxybenzoate (9 g.) was heated at 160° for 4·5 hours and then worked up as described in the case of datiscetin dimethyl ether. The phenolic product crystallised from aqueous alcohol in long, pale yellow, glistening needles, m. p. 223—224° (corr.) [Found : MeO, 12·8; loss at 90°, 7·3; in material dried at 90°; MeO, 13·8; *M* by micro-Rast, 208, 228. $C_{10}H_7O_4(OMe),H_2O$ requires MeO, 12·9; H_2O, 7·3%. $C_{10}H_7O_4(OMe)$ requires MeO, 14·0%; *M*, 222]. The substance exhibited the properties of a hydroxylated chromone and we confirmed our view of its nature by the following more rational synthesis. A mixture of ω-methoxyphloracetophenone (3 g.), fused sodium acetate (6 g.), and acetic anhydride (12 c.c.) was heated (oil-bath at 170°) for 4·5 hours, and the chromone isolated in good yield in the usual manner. After crystallisation from alcohol, the substance had m. p. 223—224° (corr.), alone or mixed with the specimen obtained from *o*-acetoxybenzoic acid.

The Occurrence of Galangin in the Root of Datisca cannabina.

The specimen labelled *datiscetin* in the Schunck Collection crystallised from aqueous alcohol in pale yellow needles, m. p. 235—240° with softening from 220°. Its behaviour with solvents, alkaline solutions, mineral acids, potassium acetate and ferric chloride in alcoholic solution closely resembled that of datiscetin and the dyeing properties of the two substances were also identical. There was, however, one striking difference in that the yellow solution in sulphuric acid, at first non-fluorescent, quickly acquired a striking violet fluorescence which was different in tone from the bluer fluorescence due to kaempferol and was entirely distinct from that due to datiscetin. The micro-analyses which we carried out led to no definite conclusion except that methoxyl groups are not present. The substance is hydrated and contains relatively less oxygen than datiscetin. It was then shown by qualitative tests that fusion with potassium hydroxide yields phloroglucinol and that picric acid is produced when the substance is boiled with nitric acid. The clue to

the nature of the material was found in the observation that galangin gives a yellow solution in sulphuric acid which soon develops a brilliant violet fluorescence that is but slightly dulled by the addition of a relatively large amount of datiscetin. The appearance of the sulphuric acid solution of a mixture of synthetical galangin and datiscetin was identical with that of the Schunck specimen dissolved in the same solvent. The following observations were then made under similar conditions: Schunck-datiscetin, m. p. 220—240°; mixed with datiscetin, m. p. 225—245°; mixed with more datiscetin, m. p. 250—260°; mixture of galangin and datiscetin, m. p. 240—255°; the last with more galangin, m. p. 223—240°; the last mixed with Schunck-datiscetin, m. p. 220—238°. A mixture of equal parts of galangin and datiscetin was crystallised from aqueous alcohol and prisms and needles were obtained. The solution was then gently heated to dissolve the needles, filtered, and allowed to cool. The apparently homogeneous needles, m. p. about 240° with previous softening, contained both galangin and datiscetin and closely resembled Schunck-datiscetin in appearance and in the fluorescence of a solution in sulphuric acid.

The authors wish to thank the Royal Society for a grant which has defrayed a part of the expense of the investigation and they also express their gratitude to the Ramsay Memorial Fellowship Trust for a Fellowship (Netherlands) which has enabled one of them to take part in the research.

THE UNIVERSITY, MANCHESTER. [*Received, June 18th*, 1925.]

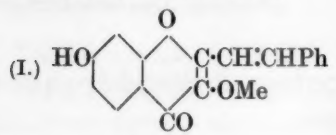
CCLXV.—*The Synthesis of certain 2-Styrylchromonol Derivatives.*

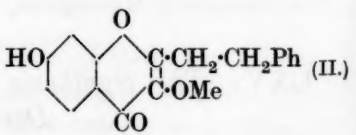
By ROBERT ROBINSON and JUNZO SHINODA.

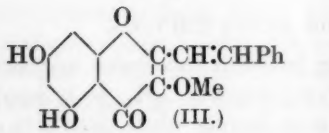
JUST as the difference in composition between successive members of the series of naturally occurring fatty acids is C_2H_4, so it would seem that the increment most common among plant products of the aromatic groups is C_2H_2. Thus benzoic acid and cinnamic acid are associated in many cases and piperic acid represents the next member of the series. Moreover, whilst methyl and propenyl or allylbenzene derivatives are of frequent occurrence, it is less usual to encounter derivatives of ethylbenzene among the constituents of plants.* For this reason we consider it probable that repre-

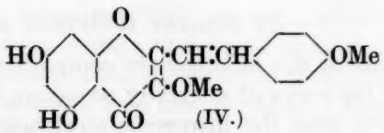
* There are, of course, exceptions to this rule, but many of the natural products with a side-chain comprising two carbon atoms have an obvious relation to more complex substances. Thus hordenine, adrenaline and mezcaline are probably derived by decarboxylation of derivatives of phenylalanine.

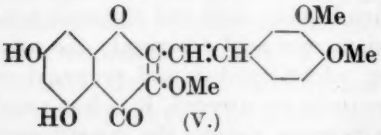
sentatives of the styrylchromones occur in nature and it may be pointed out that fukugetin, $C_{17}H_{12}O_6$ (Perkin and Phipps, J., 1904, **85**, 58), may be a tetrahydroxystyrylchromone related to luteolin, whilst pratensol, $C_{17}H_9O_2(OH)_3$ (Power and Salway, J., 1910, **97**, 231), may be similarly related to apigenin. It is significant that pratensol was found among the constituents of *Trifolium pratense* in company with undoubted flavone derivatives such as quercetin and *iso*rhamnetin, with pratol, probably a hydroxymethoxyflavone, and with a compound, $C_{15}H_7O_3(OH)_3$, isomeric with kaempferol. In the hope of making a contribution to this subject we have synthesised some styrylchromone derivatives which are, however, related to flavonols rather than to flavones. The method adopted was that indicated by Allan and Robinson (J., 1924, **125**, 2192) and utilised by Kalff and Robinson (preceding paper) in the synthesis of methylgalangin, datiscetin, and myricetin. In the simplest example a mixture of ω-methoxyresacetophenone, cinnamic anhydride, and sodium cinnamate is heated at about 180° and after hydrolysis of the product, 7-*hydroxy*-3-*methoxy*-2-*styrylchromone* (I) can be isolated. On reduction with hydrogen in presence of palladium a *dihydro*-derivative (II) is obtained, and the constitution of this substance is confirmed by its synthesis from ω-methoxyresacetophenone, β-phenylpropionic anhydride, and sodium β-phenylpropionate. In a similar manner the compounds III and IV were obtained from ω-methoxyphloracetophenone and the appropriate cinnamic acid derivatives.

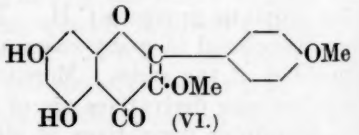












The compounds I, II, and III could be demethylated in the usual way by means of hydriodic acid and we have thus, in the last-mentioned case, obtained the styryl analogue of galangin. Unfortunately no crystalline material could be isolated from the products of demethylation of IV and V, so that we have not been

able to examine the styryl analogues of kaempferol and quercetin. Should these substances be encountered in the examination of material of natural origin, they could be recognised by means of their products of methylation under specified conditions. Both IV and V yield monomethyl ethers when shaken in aqueous alkaline solution with methyl sulphate. There can be little doubt that, as in the case of quercetin, it is the hydroxyl in position 5 which is resistant to the methylating agent. Direct comparison shows that the styryl compounds are more intensely coloured than the corresponding flavones and as mordant dyestuffs they are characterised by much greater tinctorial power. Before we were acquainted with the difficulty of demethylating the compound IV, it seemed desirable to acquire a specimen of kaempferol for purposes of comparison. The simplest plan was to adopt the new method of synthesis, and a kaempferol dimethyl ether (VI) was prepared from ω-methoxyphloracetophenone, anisic anhydride, and sodium anisate. On demethylation, kaempferol, identical with the natural product, was readily obtained. This flavonol has been previously synthesised by von Kostanecki and Tambor (*Ber.*, 1904, **37**, 792) and von Kostanecki, Lampe, and Tambor (*ibid.*, p. 2096).

Experimental.

7-Hydroxy-3-methoxy-2-styrylchromone (I).—A mixture of ω-methoxyresacetophenone (4 g.) (Slater and Stephen, J., 1920, **117**, 313), sodium cinnamate (7·5 g.), and cinnamic anhydride (16 g.) was heated (oil-bath at 180—185°) for 3 hours. The product was hydrolysed by boiling with a mixture of potassium hydroxide (8·5 g.), alcohol (100 c.c.), and a little water for 30 minutes. The alcohol was removed by distillation from the steam-bath and sufficient water added to dissolve the residue, the solution being then saturated with carbon dioxide. The yellow precipitate was crystallised several times from acetic acid and dried (4·5 g.) (Found: C, 73·4; H, 4·9. $C_{18}H_{14}O_4$ requires C, 73·5; H, 4·7%). This compound is sparingly soluble in alcohol and acetic acid and crystallises in long, pale yellow needles, m. p. 250°. It develops no coloration with alcoholic ferric chloride and its bright yellow solution in aqueous sodium hydroxide is not fluorescent. The intense yellow solution in sulphuric acid exhibits a vivid green fluorescence.

3 : 7-Dihydroxy-2-styrylchromone (corresponding with I).—The methyl ether just described was treated with an excess of boiling hydriodic acid (*d* 1·7) for 30 minutes in a stream of carbon dioxide, the mixture added to dilute sulphurous acid, and the bright yellow substance crystallised from methyl alcohol and acetic acid (Found:

C, 72·8; H, 4·5. $C_{17}H_{12}O_4$ requires C, 72·8; H, 4·2%). The woolly needles separating from methyl alcohol have m. p. 257° and the yellow solutions in aqueous sodium hydroxide and in sulphuric acid exhibit green fluorescence. The coloration with alcoholic ferric chloride is dark brownish-green. On an aluminium mordant * a bright and full lemon-yellow colour was produced, whereas 3 : 7-dihydroxyflavone exhibits very poor affinity and the silk is just coloured a pale yellow. On a chromium mordant the styryl compound gives an intense golden-yellow colour, whilst the related flavonol gives a much paler greenish-yellow. On an iron mordant both substances give a deep cinnamon-brown shade. The differences observed are not merely of intensity but also of tone. In order to obtain 3 : 7-dihydroxyflavone for this comparison we demethylated 7-hydroxy-3-methoxyflavone (Allan and Robinson, *loc. cit.*) in the usual manner by means of hydriodic acid; the product, after crystallisation from methyl alcohol, acetic acid, and finally from ethyl acetate, formed pale yellow, glistening, flat needles, m. p. 258° (Found: C, 66·4; H, 4·7; loss at 100° in a high vacuum, 6·9. $C_{15}H_{10}O_4,H_2O$ requires C, 66·2; H, 4·4; H_2O, 6·6%). von Kostanecki and Stoppani (*Ber.*, 1904, **37**, 1180) have previously obtained this substance from its 7-methyl ether, but they do not state that it crystallises with $1H_2O$.

β-*Phenylpropionic Anhydride.*—We have found the method adopted by Liebermann (*Ber.*, 1883, **21**, 3372) for the preparation of cinnamic anhydride to be expeditious and have employed it in other cases. A solution of β-phenylpropionic acid (15 g.) in acetic anhydride (30 g.) was boiled for 4 hours and then distilled; 10 g. of a viscous liquid, b. p. 216—217°/14 mm., were obtained (Found: C, 76·3; H, 6·7. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%).

7-*Hydroxy*-3-*methoxy*-2-β-*phenylethylchromone* (II).—(A) 7-Hydroxy-3-methoxy-2-styrylchromone (1 g.) dissolved in acetic acid (200 c.c.) was reduced by shaking with hydrogen, aqueous palladous chloride (10 c.c. of 1%) having been added to the mixture. Absorption ceased after about 2 hours. The product crystallised from aqueous acetic acid in colourless prisms, m. p. 186—187° (Found: C, 72·6; H, 5·5. $C_{18}H_{16}O_4$ requires C, 72·9; H, 5·4%). The yellow solution in sulphuric acid exhibits a blue fluorescence.

(B) ω-Methoxyresacetophenone (2 g.), sodium β-phenylpropionate, and β-phenylpropionic anhydride (8 g.) were mixed and heated

* All the dye-trials were made on silk. The aluminium mordant was prepared from alum and sodium carbonate and fixed with sodium silicate and it was found to be essential to exclude even traces of iron. The chromium mordant was prepared from basic chrome alum, fixed with sodium silicate, and the fabric was iron-mordanted by successive treatment with a solution of ferric nitrate and a solution containing soap and sodium carbonate.

at about 180° for 3 hours. The product, isolated as in the case of the styryl analogue, crystallised from aqueous acetic acid in colourless prisms, m. p. 186—187°, which was not depressed by admixture with the specimen prepared by the method (A).

3 : 7-*Dihydroxy*-2-β-*phenylethylchromone*, obtained by demethylation of the 3-methyl ether by means of boiling hydriodic acid, crystallises from aqueous alcohol in almost colourless, prismatic needles, m. p. 169° (Found in material dried at 100° with change of appearance: C, 68·0; H, 5·4. $C_{17}H_{14}O_4$ requires C, 68·0; H, 5·3%). The substance is readily soluble in most organic solvents and its solution in aqueous sodium hydroxide is colourless. It is devoid of any trace of mordant dyeing properties. The yellow solution in sulphuric acid exhibits a blue fluorescence and the ferric chloride coloration in alcoholic solution is dark violet.

3-*Methoxy*-5 : 7-*dihydroxy*-2-*styrylchromone* (III).—A good yield of this compound was obtained by following in every detail the method described for the preparation of 3-methoxy-7-hydroxy-2-styrylchromone. The yellow substance crystallises from acetic acid in microscopic needles, m. p. 241° (Found: C, 69·8; H, 4·6. $C_{18}H_{14}O_5$ requires C, 69·9; H, 4·5%). The orange-yellow alcoholic solution is coloured brown by the addition of a trace of ferric chloride, and the yellow solution in sulphuric acid shows a green fluorescence which becomes more intense on standing.

3 : 5 : 7-*Trihydroxy*-2-*styrylchromone* (corresponding with III).—The product of demethylation of the foregoing ether crystallised from alcohol in stellar clusters of yellow needles, m. p. 249° (Found in material dried at 100° in a high vacuum: C, 68·7; H, 4·1. $C_{17}H_{12}O_5$ requires C, 68·9; H, 4·0%). The golden-yellow solution in aqueous sodium hydroxide does not fluoresce, but the sulphuric acid solution exhibits strong fluorescence. The shades yielded by galangin on mordanted silk are almost identical with those given by 3 : 7-dihydroxyflavone, and the styryl analogue of galangin now described yields, on an aluminium mordant and on an iron mordant, shades similar to those given by 3 : 7-dihydroxy-2-styrylchromone. On a chromium mordant, however, it yields a bright orange dyeing. The *triacetyl* derivative was obtained by the action of boiling acetic anhydride in presence of fused sodium acetate on the trihydroxystyrylchromone. It crystallises from alcohol in nearly colourless, prismatic needles, m. p. 215—216°.

4-*Methoxycinnamic Anhydride*.—4-Methoxycinnamic acid was obtained in almost quantitative yield by acidification of a diluted mixture of anisaldehyde (1 mol.), malonic acid (2·5 mols.), pyridine (3 mols.), and a few drops of piperidine which had been heated on the steam-bath during 1·5 hours and then boiled. The acid crystal-

lised from boiling water in colourless, prismatic needles, m. p. 173° (recorded in the literature, 171°), and was dehydrated by vigorously boiling with three times its weight of acetic anhydride for 15 hours. After the excess of acetic anhydride and the acetic acid formed had been removed by distillation, the cooled residue solidified and could be directly employed in the chromonol synthesis. The substance crystallises from ethyl acetate in large prisms, m. p. 119—120° (Found: C, 71·3; H, 5·5. $C_{20}H_{18}O_5$ requires C, 71·0; H, 5·3%). The substitution of methoxyl for hydrogen in the *p*-position in benzoic and also in cinnamic acid has the effect of making anhydride formation by this method very noticeably more difficult. It is possible that methoxyl in the *m*-position has an influence in the other direction, since it is more easy to dehydrate veratric acid and 3 : 4-dimethoxycinnamic acid than anisic acid and 4-methoxycinnamic acid.

The following method has also been successfully employed for preparing the anhydride (compare Fischer and Freudenberg, *Ber.*, 1913, **46**, 1124). 4-Methoxycinnamic acid (5 g.) was converted into the *chloride* by gentle heating during about 25 minutes with purified thionyl chloride (25 g.) and removal of excess of the reagent by distillation in a vacuum. The crystalline chloride together with 4-methoxycinnamic acid (4 g.) was dissolved in chloroform, and pyridine (9 c.c.) gradually introduced. The anhydride crystallised and could be isolated after 3 hours by the addition of alcohol and washing with very dilute aqueous ammonia. Recrystallised from ethyl acetate, it had m. p. 119—120° (yield 8 g.).

3 : 4′-*Dimethoxy*-5 : 7-*dihydroxy*-2-*styrylchromone* (IV).—An intimate mixture of ω-methoxyphloracetophenone (4·5 g.), 4-methoxycinnamic anhydride (18 g.), and sodium 4-methoxycinnamate (9 g.) was heated at 180° in a vacuum for 3 hours, and the product hydrolysed by treatment with potassium hydroxide (10 g.) and alcohol (100 c.c.) at the boiling point for ½ hour. The yellow precipitate obtained by saturating the diluted mixture with carbon dioxide, after being washed and dried (yield 90%), crystallised from acetic acid in aggregates of intensely yellow needles, m. p. 228° (Found: C, 66·7; H, 4·2. $C_{19}H_{16}O_6$ requires C, 67·0; H, 4·2%). The orange solution in sulphuric acid exhibits greenish-yellow fluorescence and the yellow solution in alcohol develops a brown coloration with ferric chloride.

3 : 7 : 4′-*Trimethoxy*-5-*hydroxy*-2-*styrylchromone*, the methyl ether of the substance described in the last section, was obtained by shaking the red solution of the phenol in aqueous sodium hydroxide with methyl sulphate until the yellow precipitate no longer dissolved on the addition of more sodium hydroxide. The product was

collected, washed with water, and crystallised from aqueous acetic acid, separating in bright yellow prisms, m. p. 156° (Found: C, 67·6; H, 5·0. $C_{20}H_{18}O_6$ requires C, 67·8; H, 5·1%). This substance is quite insoluble in aqueous sodium hydroxide, even when boiled, but the intensification of the colour from yellow to orange in alcoholic solution on the addition of solid potassium hydroxide indicates the weak phenolic function. It is curious that on diluting such an alcoholic solution with water a clear yellow liquid is obtained and the phenol actually separates completely on boiling, leaving a colourless solution. The alcoholic solution gives a yellowish-brown coloration on the addition of ferric chloride.

3 : 4-*Dimethoxycinnamic Anhydride*.—3 : 4-Dimethoxycinnamic acid is obtained in almost quantitative yield from veratraldehyde by condensation with malonic acid in pyridine–piperidine solution at 100° and it may also be conveniently prepared by the methylation of ferulic acid which is effected by shaking an aqueous alkaline solution with methyl sulphate. Ferulic acid was produced in 80% yield when a mixture of vanillin (50 g.), malonic acid (104 g.), pyridine (140 c.c.), and piperidine (4 c.c.) was heated for 1·5 hours on the steam-bath. The acid, crystallised from hot water, had m. p. 171° (recorded in the literature, 168—169°). A mixture of 3 : 4-dimethoxycinnamic acid (5 g.) and acetic anhydride (10 g.) was vigorously boiled for 5 hours and the acetic acid and excess of acetic anhydride removed by distillation in a vacuum. The residue was dissolved in a little hot benzene and, on cooling, the new anhydride separated. It crystallised from ethyl acetate in colourless needles, m. p. 174—175° (Found: C, 66·4; H, 5·8. $C_{22}H_{22}O_7$ requires C, 66·3; H, 5·5%).

3 : 3′ : 4′-*Trimethoxy*-5 : 7-*dihydroxy*-2-*styrylchromone* (V).—The method of preparation of this substance from ω-methoxyphloracetophenone, 3 : 4-dimethoxycinnamic anhydride, and sodium 3 : 4-dimethoxycinnamate followed exactly the lines of the similar cases described above. The bright yellow substance is readily soluble in alcohol and acetic acid, but may be crystallised from methyl alcohol in fine orange needles (Found: C, 61·7; H, 5·2; loss at 100° in a high vacuum, 5·3. $C_{20}H_{18}O_7,H_2O$ requires C, 61·8; H, 5·3; H_2O, 4·9%). The dried material is yellow and has m. p. 233—234°. The orange solution in sulphuric acid exhibits a weak green fluorescence; the ferric chloride reaction in alcoholic solution is brown; and the alkaline solutions are orange-yellow.

3 : 7 : 3′ : 4′-*Tetramethoxy*-5-*hydroxy*-2-*styrylchromone*.—The phenol last described was mixed with a little water and treated alternately with concentrated potassium hydroxide and methyl sulphate until the solution was no longer red when alkaline. The yellow precipitate

crystallised from alcohol and from ethyl acetate in glistening, yellow leaflets, m. p. 203—204° (Found: C, 65·3; H, 5·2. $C_{21}H_{20}O_7$ requires C, 65·6; H, 5·2%). The behaviour of this compound with aqueous and alcoholic solutions of alkali metal hydroxides and with ferric chloride closely resembled that of 3 : 7 : 4′-trimethoxy-5-hydroxy-2-styrylchromone.

3 : 4′-*Dimethoxy*-5 : 7-*dihydroxyflavone* (VI).—Anisic acid is not completely dehydrated by boiling acetic anhydride in 6 hours, but in 20 hours a good yield of the anhydride is obtained and the process is convenient. The substance isolated as in the example previously described, crystallised from ethyl acetate in needles, m. p. 98—99° (compare Pisani, *Annalen*, 1857, **102**, 284). The preparation of a flavonol derivative from ω-methoxyphloracetophenone (2·5 g.), anisic anhydride (10 g.), and sodium anisate (5 g.) was carried out as in previous cases. The crude product crystallised from aqueous acetic acid in pale yellow platelets with rounded corners, m. p. 234°. The substance exhibits a bronze-like appearance (Found: C, 65·1; H, 4·6. $C_{17}H_{14}O_6$ requires C, 65·0; H, 4·4%). This kaempferol dimethyl ether is sparingly soluble in hot methyl alcohol and gives a violet ferric chloride reaction in alcoholic solution. Its yellow solution in concentrated sulphuric acid exhibits a bright bluish-green fluorescence the intensity of which increases on standing. On demethylation with hydriodic acid (*d* 1·7) in the usual manner, kaempferol was readily obtained. The pale yellow needles deposited from alcoholic solution had m. p. 276—277° and this is the m. p. given by A. G. Perkin (J., 1902, **81**, 585), whereas von Kostanecki and Gordin quote the value 271° (*Ber.*, 1901, **34**, 3723) and von Kostanecki, Lampe, and Tambor (*loc. cit.*) give the m. p. 275° for the synthetical material. The strong greenish-blue fluorescence of the yellow solution in sulphuric acid was observed and the dyeing and other properties were those of kaempferol. The *tetra-acetyl* derivative was prepared and after crystallisation from ethyl alcohol had m. p. 181—182°, but, as stated by A. G. Perkin, when crystallised from methyl alcohol the substance sinters at 116—120° without completely melting, then hardens on further heating and melts at 181—182°. These observations render it certain that the synthetical material is identical with the naturally occurring flavonol called kaempferol.

We desire to thank the Royal Society for a grant which has defrayed a part of the cost of this investigation.

THE UNIVERSITY, MANCHESTER. [*Received, June 23rd*, 1925.]

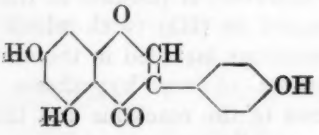
CCLXVI.—*Synthetical Experiments in the* iso*Flavone Group. Part I.*

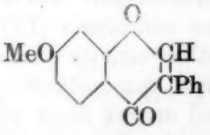
By WILSON BAKER and ROBERT ROBINSON.

WHILST derivatives of 2-phenylchromone (flavone) and related substances in various states of oxidation (catechins, cyanomaclurin, butein, hyssopinaglykone, the anthocyanins and anthoxanthins) are found widespread in nature, the occurrence of derivatives of 3-phenylchromone (*iso*flavone) has not yet been definitely proved in any single instance. Nevertheless Finnemore has suggested (*Pharm. J.*, 1910, **31**, 604) that prunetin, $C_{16}H_{12}O_5$, obtained by hydrolysis of the glucoside prunetrin is the methyl ether of a trihydroxy*iso*flavone (I) and the isolation of *p*-hydroxyphenylacetic acid and phloroglucinol from the products of fusion with potassium hydroxide is strong evidence that this view is correct. On demethylation prunetin yields prunetol, $C_{15}H_{10}O_5$, and we are informed by Professor A. G. Perkin that there is a possibility that this substance is identical with genistein, the colouring matter of Dyer's Broom (*Genista tinctoria*) (Perkin and Newbury, J., 1899, **75**, 830; Perkin and Horsfall, J., 1900, **77**, 1310). The following comparison will serve to make clear the basis of this suggestion. Genistein; long, colourless needles from aqueous alcohol, m. p. 291—293°; prunetol, colourless needles from aqueous alcohol, m. p. *ca.* 290° (decomp.): triacetylgenistein, m. p. 197—201°; triacetylprunetol, m. p. 205°: genistein dimethyl ether, colourless leaflets from alcohol, m. p. 137—139°; prunetin monomethyl ether, flat needles, m. p. 145°: acetyl derivative of genistein dimethyl ether, colourless needles, m. p. 202—204°; acetyl derivative of prunetin monomethyl ether, colourless needles, m. p. 202°. In addition it was found that genistein dimethyl ether yields *p*-methoxyphenylacetic acid by hydrolysis with alcoholic potassium hydroxide.

A synthesis of the compound (I) would clearly be of considerable interest and we have decided to attempt it. The present communication is a record of the necessary preliminary investigation of the methods available, and it has been found that though *iso*flavones substituted in position 2 are easy to prepare, the contrary is the case when it is desired to leave this position unsubstituted.

(I.)

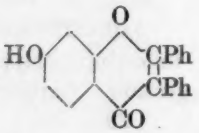


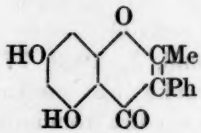


(II.)

The problem is analogous to that presented by the synthesis of

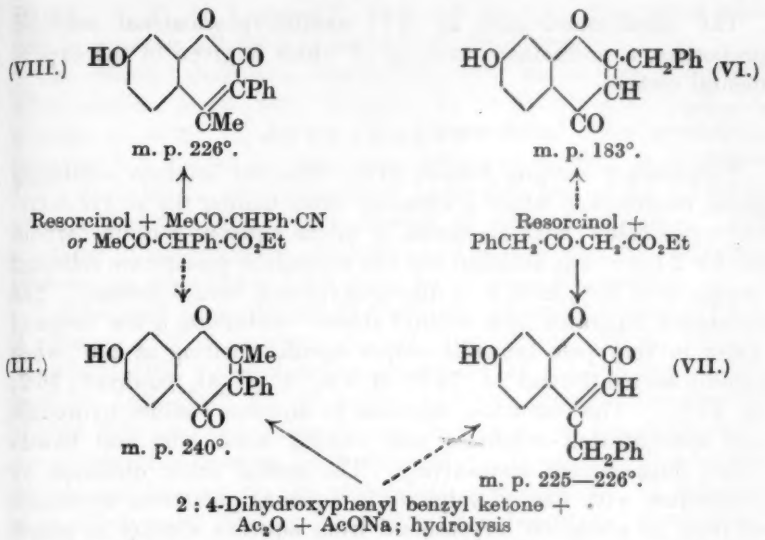
anhydrobrazilic acid, which is also a 3-substituted chromone derivative, but the method which was successful in that case (Perkin and Robinson, J., 1908, **93**, 503) was found to be inapplicable in the present instance. Ultimately 7-methoxy*iso*flavone (II) was synthesised by degradation of its 2-styryl derivative (X) by oxidation with potassium permanganate in pyridine solution and thermal decomposition of the resulting 7-methoxy*iso*flavone-2-carboxylic acid. A synthesis of (I) is thus rendered feasible. 2-Substituted *iso*flavones are quite readily obtained by the interaction of 2 : 4-dihydroxyphenyl benzyl ketone or the corresponding phloroglucinol derivative with a mixture of the anhydrides and sodium salts of carboxylic acids at 170—180° in accordance with a general method. For example, interaction of the former ketone and acetic anhydride and sodium acetate followed by hydrolysis of the product yields 7-*hydroxy*-2-*methyl*iso*flavone* (III), 7-*hydroxy*-3-*phenyl*-*flavone* (IV) is similarly obtained by means of benzoic anhydride and sodium benzoate, whilst 2 : 4 : 6-trihydroxyphenyl benzyl ketone, acetic anhydride, and sodium acetate yield ultimately the iso*flavone* (V).

(IV.) 



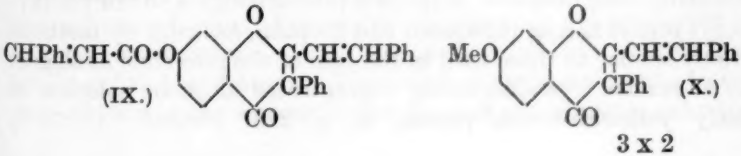
(V.)

A substance which, it was claimed, had the formula (III) has been obtained by Ghosh (J., 1916, **109**, 105) and formulæ (IV) and (V) have been assigned by Jacobson and Ghosh (J., 1915, **107**, 1051) to compounds prepared by them, but the properties of the substances as recorded by these authors do not tally, even approximately, with our observations and there appears to be no possibility that the specimens prepared by the two methods can be identical. Since the synthetical process employed by Ghosh and by Jacobson and Ghosh is essentially that due to von Pechmann and was originally devised for the synthesis of coumarins, it seems possible that all these compounds, including eleven alleged *iso*flavones, are α-pyrones. In regard to the three substances already mentioned, this conclusion is inevitable unless it can be shown that we have taken a wrong view of the course of the reactions described in this communication. No alternative, however, is possible in the case of the compound (IV) and in regard to (III) (with which V is doubtless strictly analogous) the relations included in the annexed scheme demonstrate the correctness of our hypothesis. The dotted arrows show possible courses of the reactions and the full arrows the direction in which they actually proceed :



The condensation of ethyl β-keto-γ-phenylbutyrate and resorcinol yields 7-*hydroxy*-4-*benzylcoumarin* (VII), because the product of the reaction is not identical with the 7-hydroxy-2-benzylchromone (VI) synthesised by Hannach and Kostanecki (*Ber.*, 1902, **35**, 867). The non-identity of (III) and (VII) disposes of the only alternative for (III) and therefore the compound obtained by Ghosh from acetylphenylacetonitrile and resorcinol must have the constitution (VIII). It is possible that the whole of the compounds described by Jacobson and Ghosh and by Ghosh in four papers (*loc. cit.* and J., 1915, **107**, 424, 959) as γ-pyrones are in fact α-pyrones. A further critical examination of this subject is in progress. The question of the mechanism of the chromone synthesis is to some extent answered as the result of the observation that the di-*o*-acetyl derivative of 2 : 4-dihydroxyphenyl benzyl ketone, which is stable to acetic anhydride alone, suffers ring closure under the influence of acetic anhydride and sodium acetate.

The action of cinnamic anhydride and sodium cinnamate (compare the preceding paper) on 2 : 4-dihydroxyphenyl benzyl ketone gave rise to 7-*cinnamoyloxy*-2-*styryl*iso*flavone* (IX), from which (X) and then, as already stated, (II) were derived. The investigation is being extended.



The alkali-metal salts of (IV) exhibit phenomenal colloidal properties, a preliminary account of which is given in the experimental section.

EXPERIMENTAL.

7-Hydroxy-2-methylisoflavone (III).—The red solution exhibiting green fluorescence which is obtained after boiling the acetyl derivative (see below) with an excess of dilute aqueous sodium carbonate for 2 hours was acidified and the crystalline precipitate collected (yield—over 90% from 2 : 4-dihydroxyphenyl benzyl ketone). The substance separates from methyl alcohol containing a few drops of water in very pale brownish-yellow needles melting at 240° when rapidly heated (Found : C, 76·3; H, 4·8. $C_{16}H_{12}O_3$ requires C, 76·2; H, 4·8%). The colourless solutions in aqueous sodium hydroxide and concentrated sulphuric acid exhibit weak blue and bluish-violet fluorescences respectively. The *methyl* ether obtained by interaction with methyl sulphate in aqueous potassium hydroxide solution at about 60° crystallised from aqueous alcohol in nearly colourless needles, m. p. 135·5° (Found : C, 76·7; H, 5·3. $C_{17}H_{14}O_3$ requires C, 76·7; H, 5·3%). The *acetyl* derivative was prepared by heating (oil-bath at 170—180°) a mixture of 2 : 4-dihydroxyphenyl benzyl ketone (10 g.) (Chapman and Stephen, J., 1923, **123**, 404), acetic anhydride (40 c.c.), and anhydrous sodium acetate (10 g.) under reflux for 12 hours. The product was shaken with dilute hydrochloric acid, and the solid crystallised from alcohol in colourless prisms, m. p. 162° (Found : C, 73·6; H, 4·8. $C_{18}H_{14}O_4$ requires C, 73·4; H, 4·8%). The same compound was obtained from 2 : 4-diacetoxyphenyl benzyl ketone (Chapman and Stephen, *loc. cit.*) in a precisely similar manner.

7-Hydroxy-4-benzylcoumarin (VII).—A solution of resorcinol (2 g.) and ethyl β-keto-γ-phenylbutyrate (2 g.) (Attwood, Stevenson, and Thorpe, J., 1923, **123**, 1762) in concentrated sulphuric acid (10 c.c.) was heated on the steam-bath for 20 minutes. The solid isolated after the addition of water crystallised from alcohol in faintly brown prisms, m. p. 225—226° (Found : C, 76·2; H, 4·9. $C_{16}H_{12}O_3$ requires C, 76·2; H, 4·8%). The yellow solution in aqueous sodium hydroxide has a blue fluorescence and the colourless solution in sulphuric acid fluoresces bluish-violet.

5 : 7-Dihydroxy-2-methylisoflavone (V).—This substance and its derivatives were obtained, in the first place from 2 : 4 : 6-trihydroxyphenyl benzyl ketone (Chapman and Stephen, *loc. cit.*), by methods entirely similar to those used in the case of the resorcinol analogue. The substance crystallises from concentrated alcoholic solution in faintly yellowish-brown prisms, m. p. 228° (Found : C, 71·7;

H, 4·7. $C_{16}H_{12}O_4$ requires C, 71·6; H, 4·5%). The yellow solution in aqueous alkalis does not exhibit fluorescence.

The *diacetyl* derivative crystallises from alcohol in colourless, silky needles, m. p. 169° (Found: C, 68·0; H, 4·6. $C_{20}H_{16}O_6$ requires C, 68·2; H, 4·6%). The 7-*monomethyl* ether crystallises from methyl alcohol in glistening, colourless needles, m. p. 186—187°, insoluble in aqueous sodium hydroxide but giving a bluish-green coloration with ferric chloride in alcoholic solution. The solutions in concentrated sulphuric acid of this and the two substances last described exhibit weak bluish-green fluorescence.

7-*Hydroxy*-3-*phenylflavone* (7-*Hydroxy*-2-*phenylisoflavone*) (IV).—A mixture of 2 : 4-dihydroxyphenyl benzyl ketone (20 g.), benzoic anhydride (100 g.), and sodium benzoate (10 g.) was heated (oil-bath at 180—190°) for 12 hours, and the product dissolved in alcohol (250 c.c.) and water (50 c.c.) by heating on the steam-bath. A solution of potassium hydroxide (60 g.) in water (100 c.c.) was added, and heating on the steam-bath continued for 15 minutes, after which water (500 c.c.) was added and the phenol precipitated by saturating the solution with carbon dioxide. It is important to follow the above directions in order to ensure the avoidance of the formation of a thick gel through which the gas cannot be passed. The crude product crystallised from ethyl alcohol (800 c.c.) in microscopic needles and on recrystallisation separated in glistening, pale yellow plates, m. p. 270—271° (yield of fully purified material, 20 g.) (Found: C, 80·3; H, 4·6. $C_{21}H_{14}O_3$ requires C, 80·2; H, 4·5%). The pale yellow solution in sulphuric acid exhibits a bluish-green fluorescence. The substance does not appear to dissolve in cold aqueous potassium hydroxide, but this is due to the formation of a gel round each crystal. On heating, a greenish-yellow solution is produced and this sets on cooling to a clear gel. A 1% solution sets to a stiff gel which is with difficulty shaken from a test-tube, whilst even a 0·1% solution gives a weak gel which, with an excess of alkali, will almost permit the inversion of the tube without displacement of the contents. The nature of the gels is very much affected by the concentration of the alkali. The *acetyl* derivative, prepared from the phenol by the action of boiling acetic anhydride for 4 hours, crystallised from acetic acid in pale yellow prisms, m. p. 208—209° (Found: C, 77·4; H, 4·5. $C_{23}H_{16}O_4$ requires C, 77·5; H, 4·5%).

7-*Cinnamoyloxy*-2-*styrylisoflavone* (IX).—A mixture of 2 : 4-dihydroxyphenyl benzyl ketone (10 g.), cinnamic anhydride (40 g.), and sodium cinnamate (10 g.) was heated (oil-bath at 170—180°, finally at 215°) for 5 hours. The cooled, ground product was washed with dilute aqueous sodium hydroxide, and the cinnamic anhydride

decomposed by heating on the steam-bath for an hour with alcohol (100 c.c.), water (20 c.c.), and concentrated sulphuric acid (1 c.c.). The solid then obtained on the addition of water was collected, washed with aqueous sodium hydroxide, and crystallised from acetic acid, in which it was sparingly soluble. The pale yellowish-brown prisms, m. p. 213—214°, dissolved in sulphuric acid to an intensely yellow solution exhibiting green fluorescence (Found: C, 81·6; H, 4·8. $C_{32}H_{22}O_4$ requires C, 81·7; H, 4·7%).

7-*Methoxy*-2-*styryl*isoflavone (X).—The crude cinnamoyloxystyryl*iso*flavone from 10 g. of 2 : 4-dihydroxyphenyl benzyl ketone was added to alcohol (100 c.c.) and potassium hydroxide (7·5 g.) dissolved in a little water, and the whole heated for 5 minutes on the steam-bath. Water (100 c.c.) * was added and the phenol contained in the solution was methylated at 60° by the alternate addition of methyl sulphate and concentrated aqueous potassium hydroxide. After the addition of more water the methyl ether was collected (13·9 g.). It crystallised from ethyl alcohol, in which it was sparingly soluble, in pale yellow needles, m. p. 204—205° (Found: C, 81·4; H, 5·0. $C_{24}H_{18}O_3$ requires C, 81·3; H, 5·1%). The deep yellow solution in sulphuric acid has a green fluorescence.

7-*Methoxy*isoflavone (II).—7-Methoxy-2-styryl*iso*flavone (2 g.) dissolved in pure pyridine (20 c.c.) was oxidised at 0° in the course of an hour by the slow addition, with stirring and passage of carbon dioxide, of aqueous potassium permanganate (100 c.c. saturated at 15°). The manganese precipitate was brought into solution by sulphur dioxide and after the addition of dilute hydrochloric acid the ether-soluble contents of the liquid were isolated. The crude product was extracted with warm sodium bicarbonate solution, the filtrate acidified, and the organic acids were again collected by ether. The residue mixed with a little copper powder was cautiously heated over a free flame until evolution of carbon dioxide ceased, and the product shaken with aqueous sodium bicarbonate and ether. The neutral oil obtained from the ethereal solution solidified on stirring and the substance crystallised from not too much alcohol in needles, m. p. 155° (Found: C, 75·7; H, 5·1. $C_{16}H_{12}O_3$ requires C, 76·1; H, 4·8%). The colourless solution in sulphuric acid exhibits a blue fluorescence.

The authors desire to thank the Chemical Society for a grant which has defrayed a part of the cost of this investigation.

THE UNIVERSITY, MANCHESTER. [*Received, June 23rd,* 1925.]

* If more water is added, a thick, mucilaginous, colloidal solution results.

CCLXVII.—*Oxidation Products of Oleic Acid. Part II. Degradation of Dihydroxystearic Acid.*

By ARTHUR LAPWORTH and EDWARD NEVILLE MOTTRAM.

SPIRONDONOV (*J. Russ. Chem. Soc.*, 1887, **19**, 646) oxidised dihydroxystearic acid with potassium permanganate, and an examination of the degradation products led to the separation of *n*-octoic, suberic and azelaic acids. Edmed (J., 1898, **73**, 628) carried out further investigations in this direction, but obtained no evidence of the formation of either suberic or *n*-octoic acid. He isolated three main products, namely azelaic, *n*-nonoic and oxalic acids, and assumed that the last-named was produced by the oxidation of the chain of carbon atoms which otherwise would have yielded pelargonic acid. Edmed's conclusion has been generally accepted, but the evidence obtained by the present authors does not support his view. In dilute alkaline solution at the ordinary temperature, *n*-octoic, suberic, and oxalic acids are the main oxidation products in several experiments, and it is necessary to conclude that the oxalic acid is a primary product in the degradation of dihydroxystearic acid and is formed by a splitting between the 8—9 and 10—11 carbon atoms as indicated below.

$$CH_3\cdot[CH_2]_6\cdot CH_2\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot[CH_2]_6\cdot CO_2H$$

$CH_3\cdot[CH_2]_6\cdot CO_2H$	$CO_2H\cdot CO_2H$	$CO_2H\cdot[CH_2]_6\cdot CO_2H$
n-Octoic acid.	Oxalic acid.	Suberic acid.

In the conditions employed by Edmed, it appears that this mode of oxidation takes place simultaneously with that of the better known type

$$CH_3\cdot[CH_2]_7\cdot CH(OH)\cdot CH(OH)\cdot[CH_2]_7\cdot CO_2H$$

$CH_3\cdot[CH_2]_7\cdot CO_2H$	$CO_2H\cdot[CH_2]_7\cdot CO_2H$
n-Nonoic acid.	Azelaic acid.

EXPERIMENTAL.

1. (a) *Oxidation.* A solution of dihydroxystearic acid (5·0 g.) and caustic soda (10 g.) in water (1000 c.c.) was cooled, ice-cold water (3000 c.c.) added, and the whole well shaken during the addition of 1% aqueous potassium permanganate (2000 c.c.). Oxidation having proceeded at the ordinary temperature for 2½ hours, the solution was decolorised by sulphur dioxide, concentrated hydrochloric acid (100 c.c.) added, and the white, flocculent precipitate of unchanged dihydroxystearic acid filtered off, and washed with water. Traces of liquid fatty acids were removed from the drained

precipitate by washing with a little light petroleum (b. p. 40—60°) and the unchanged dihydroxystearic acid (0·40 g., m. p. 130°) was recovered.

The aqueous filtrate was neutralised with sodium carbonate, concentrated to about 500 c.c., and excess of hydrochloric acid added. The liberated mixed acids, isolated by means of ether,* were distilled with steam to separate the volatile portion; on cooling, the aqueous solution (75 c.c.) in the distillation flask deposited 1·6 g. of crystalline suberic acid, m. p. 137—138°. The mother-liquor on evaporation yielded further small quantities of suberic acid (0·3 g.). The total yield of suberic acid obtained was 1·90 g. (Theory requires 2·47 g.) and the equivalent found was 87·9 ($C_8H_{14}O_4$ requires 87·0), this slightly high value being almost certainly due to traces of octoic acid.

(b) *Examination of dibasic acid for azelaic acid.* The whole of the dibasic acid was warmed with 20—30 c.c. of ether, and the solution allowed to crystallise. The solid which separated (1·5 g.) was removed by filtration, and the mother-liquor evaporated to dryness. This solid was dissolved in water and treated with magnesium carbonate. (The magnesium salt of azelaic acid is much less soluble in water than that of suberic acid.) The most insoluble fraction of magnesium salt was treated with dilute hydrochloric acid, and the free dibasic acid extracted with ether. The acid obtained in this way melted at 139°, so that more than traces of azelaic acid could not have been present.†

(c) *Isolation of monobasic acid formed.* The aqueous distillate containing the liquid fatty acid was extracted with petroleum (b. p. 40—60°), and the solution dried with sodium sulphate. The liquid left after recovering solvent was freed from traces of petroleum by gently warming under reduced pressure and on cooling to 9° the acid solidified in colourless laminæ, m. p. 14°; the yield of monobasic acid was 1·4 g. (Theory for octoic acid is 2·05 g.) In conjunction with the results mentioned in the footnote,‡ these observations show that the greater part of the monobasic acid was octoic acid.

(d) *Estimation of oxalic acid formed.* The calcium oxalate precipi-

* The light petroleum washings from unchanged dihydroxystearic acid were reserved and added to the ethereal solution of oxidation products.

† In another experiment, the dibasic acid (6·5 g.) obtained from a larger quantity of dihydroxystearic acid was examined according to the above method and no azelaic acid was detected.

‡ In another experiment, starting from 16 g. of dihydroxystearic acid, 4·75 g. of fluid fatty acid distilled steadily at 233—235° at ordinary pressure. (Octoic acid boils at 236–237° and nonoic acid at 253–254°.) The equivalent found was 142·2; $C_8H_{16}O_2$ requires 144·0.

tated from the aqueous liquor from (c), made alkaline with ammonia, by the addition of calcium sulphate solution, was collected after 12 hours and treated with warm acetic acid. The residue was washed with water, and the oxalic acid estimated by titration with 1% potassium permanganate at 60° (Found : 0·86 g. ; calc., 1·28 g.). This quantitative result is, however, not offered with the same degree of confidence as those for octoic and suberic acids.

Oxidation of Dihydroxystearic Acid by Edmed's Method.—To a hot solution of dihydroxystearic acid (6·0 g.) in 150 c.c. of 1% caustic potash, 8·2 g. of potassium permanganate dissolved in 450 c.c. of water were added and oxidation was continued until the potassium manganate first formed was completely reduced (about 10 minutes). Manganese dioxide was filtered off, the filtrate acidified with sulphuric acid, and unchanged dihydroxystearic acid (3·0 g.) was filtered off. The oxidation products were isolated from the filtrate as in the above experiments.

The extracted dibasic acid (1·3 g.) was treated with cold ether, and the more soluble fraction (0·9 g.) converted into magnesium salt as in 1 (b) above. The most insoluble fraction of the latter yielded almost pure azelaic acid (m. p. 105°) (Equivalent found, 93·8; required, 94·0).

The fraction of dibasic acid less soluble in ether melted at 137—138° and had the equivalent 87·5. It was therefore mainly suberic acid.

Conclusions.—(1) The oxidation of dihydroxystearic acid by the method described in 1 (a) therefore leads to the formation of : suberic acid, in amount at least 80% of the theoretical; octoic acid, in amount at least 70% of the theoretical; and oxalic acid.

(2) By Edmed's original method, both suberic and azelaic acid are formed.

This work was carried out in continuation of researches begun under the auspices of the Food Investigation Board of the Department of Scientific and Industrial Research.

A grant from the Department of Scientific and Industrial Research to one of us (E. N. M.) rendered it possible for him to take part in the research and is gratefully acknowledged.

THE UNIVERSITY, MANCHESTER. [*Received, July 4th,* 1925.]

CCLXVIII.—*The Effect of Ultra-violet Light on Dried Hydrogen and Oxygen.*

By HERBERT BRERETON BAKER and MARGARET CARLTON.

IN 1922 Coehn and Tramm (*Ber.*, **56**, 455), working with an "electrolytic" mixture of hydrogen and oxygen, found that the gases interacted at the same rate when exposed to the light from a quartz mercury lamp whether they were dry or moist. This conclusion, if confirmed, would have an important bearing on the theory of the determining effect of water vapour. It was thought necessary to repeat the experiments, since these authors had not succeeded in attaining the same degree of resistance to the effect of heat on the dried gases as had been attained by one of us (Baker, J., 1902, **81**, 400). In these experiments, it was shown that the highly dried, "pure" gas mixture could be heated to redness and a silver wire melted in it without measurable action. Coehn and Tramm have succeeded in obtaining the gases so pure and dry that no explosion took place on heating to redness, but slow combination only. It is impossible to say why their gases did not give the same results as those described in 1902. Their work, as described, seems to have been most carefully carried out. The only point in their apparatus to which objection might be taken is the presence of two greased taps. The interaction of hydrogen and oxygen is one of those most susceptible to the slightest trace of impurity; it is possible that a few molecules of vapour from the lubricant used may have produced a diminution in the resistance to chemical action.

In our experiments the gases were produced by the electrolysis of a solution of barium hydroxide which had been recrystallised fifteen times. The reaction tubes were of the clearest fused quartz bent into L shape. The shorter arm was closed. The tubes were boiled in a mixture of chromic and nitric acids; after washing with distilled water, they were roughly dried in an electric oven and heated to bright redness after being exhausted. Air dried by phosphorus pentoxide was admitted after heating, the process being repeated six times.

The tubes were then filled with highly purified and dried mercury and the gaseous mixture was admitted over a mercury trough. It had been found, in the previous work, that the gases evolved during the electrolysis were not as resistant to chemical action in the first as in the later stages. The gaseous mixture was therefore allowed to escape during 3 days before being collected in the quartz tubes. Pairs of tubes, similar in diameter and in shape,

were filled at the same time. Into one of the pair was introduced a plug of phosphorus pentoxide which had been distilled in oxygen, the other being left in the undried condition. Both tubes, mounted on a special stand, were left in the dark room during the time specified.

The pair of tubes was then arranged symmetrically near a quartz mercury vapour lamp, so that both were exposed, as nearly as possible, to the same radiation. The part of the tube containing the phosphorus pentoxide was shielded from the direct rays of the lamp. The amount of chemical action was estimated by measurement of the rise of the mercury column in each tube, the temperature and pressure being noted at the same time.

In all, six pairs of tubes have been tested, prepared in the same way but with different lengths of time allowed for drying. In every case, there was a marked difference between the wet and the dry tubes, the latter showing in some cases no measurable action.

The following table is a summary of the results.

	Period of drying.	Time of exposure to light (hours).	Rise in mercury column (mm.). Dry.	Wet.
1	2 weeks	7	4	14
2	3 weeks	5	4	30
	After 12 hours' interval	6	9	43
3	4 weeks	5	0	6·1
	After 12 hours' interval	3	1	4·5
	After 12 hours' interval	5	6·5	7·2
4	7 weeks	$6\frac{1}{4}$	0	2·3
	After 12 hours' interval	$6\frac{1}{2}$	0·35	6·5
5	8 weeks	5	0·5	5
	After 12 hours' interval	5	0·1	5
6	8 weeks	5	0	6·1
	After 12 hours' interval	6	0	6·2
	After 12 hours' interval	9	0·5	9·1
	After 12 hours' interval	$8\frac{1}{2}$	1·5	10
	After 12 hours' interval	6	10	12·5

Note, added August 1st.—One tube, dried for 12 weeks, was exposed at a distance of 2 cm. from the quartz mercury lamp for 13 hours without showing any measurable contraction.

It should be noticed that during the 12-hour intervals renewed drying is taking place, so that it is probable that only a fraction of the water produced (if any) during a day's exposure is available for promoting the chemical action on the next day.

It is also noticeable that in experiments 3 and 6 there is a sudden rise in the amount of gas combined in the dry tubes. This seems to be due to the amount of water formed during the previous day being too great to be absorbed by the drying agent during the night, so that the gases start in a comparatively moist condition.

It was found impracticable to leave the lamp running all night,

as it had a tendency, after some hours' run, to go out. On two occasions it was found that an exposure of 5 hours to the light had produced no action in either the wet or the dry tube. On examination it was found that a purple film had formed on the inside of the quartz tube of the lamp. Professor R. Wood (*Proc. Roy. Soc.*, 1924, *A*, 688) noticed the same phenomenon and he recommended the opening of the tube and the polishing of the interior with rouge. We found, however, that the full activity of the lamp could be restored by strongly heating the quartz tube of the lamp with a hot bunsen burner.

It was noteworthy that, in none of the tubes, wet or dry, was any tailing of the mercury observed; ozone therefore was not formed. The loss of mobility of mercury exposed to ozone forms one of the most delicate tests known. In two cases, both of wet tubes, a yellow film was formed. This proved to be mercuric oxide and amounted in the one tube in which it was determined to 4·1 mg. Its formation could not have been due to ozone, which produces mercurous oxide, never mercuric oxide.

Professor Bone (private communication) considers that phosphorus pentoxide cannot exert its full drying power when its temperature is allowed to rise above 25°. In the experiments described above, the gases generally reach a temperature of above 30°. In two of them the part of the tube containing the pentoxide was kept surrounded by ice during the whole of the run. The rate of union was not found to be altered by this treatment.

We wish to express our thanks to Messrs. Brunner Mond and Co. for a grant for the purchase of apparatus.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, July 4th*, 1925.]

CCLXIX.—*Imino-aryl Ethers. Part III. The Molecular Rearrangement of N-Phenylbenziminophenyl Ether.*

By ARTHUR WILLIAM CHAPMAN.

IT is on record (Mumm, Hesse, and Volquartz, *Ber.*, 1915, **48**, 379) that benzoyldiphenylamine (II) may be obtained by heating *N*-phenylbenziminophenyl ether (I) at 240° for 1 hour.

$$\text{(I.)}\quad \text{PhO·CPh:NPh} \xrightarrow{\text{heat}} \text{O:CPh·NPh}_2 \quad \text{(II.)}$$

On repeating this experiment, unchanged material only could be recovered. However, benzoyldiphenylamine was obtained

after heating at 270—300° for 2 hours. The transformation had apparently occurred completely and without the formation of by-products, and therefore merited further investigation, especially as no quantitative study seems to have been made of any of the isomeric changes among imino-ethers of the aliphatic series and imino-esters (Pinner, "Die Imidoaether," 1892; Wislicenus and Goldschmidt, *Ber.*, 1900, **33**, 1470; Lander, J., 1903, **83**, 406; Wheeler and Johnson, *Amer. Chem. J.*, 1903, **30**, 24; Busch, Blume, and Pungs, *J. pr. Chem.*, 1909, **79**, 513; Kuhara, *Cent.*, 1911, I, 1514; Short and Smith, J., 1922, **121**, 1803).

The dynamics of the reaction were first studied. The purified imino-ether was heated in a thermostat maintained at various temperatures between 220° and 300°, and the product was submitted to thermal analysis (Hollemann, "Direkte Einfuhrung von Substituenten in den Benzolkern," 1910, p. 26). The freezing-point curve of mixtures of the two components was drawn from the following observations on mixtures of *N*-phenylbenziminophenyl ether with known quantities (*a*) of benzoyldiphenylamine.

a%	20	30	40	50	60	70	80	90	95	100
F. p. ...	107·8°	123·8°	134·8°	144·8°	152·7°	159·7°	165·6°	171·6°	174·6°	176·7°

The freezing points of mixtures containing less than 20% of benzoyldiphenylamine could not be determined accurately.

The progress of the transformation agreed closely with that required by the unimolecular formula; a typical series of observations is the following, t being the time of heating in minutes, x the percentage of benzoyldiphenylamine formed, and the temperature 262°:

t	32	60	120	181	240	300	360	
x	33	54	80	90	94	98	99·5	
$k \times 10^3$	5·4	5·6	5·8	5·5	5·1	5·7	5·6	Mean 5·5

The velocity coefficients at different temperatures are:

Temp.	228°	246—247°	262°	272°	278°	282°	287—288°	292—293°
$k \times 10^3$	0·1—0·2	1·6	5·5	11	18	23	34	45

The mean temperature coefficient between 246° and 292° was 2·06 per 10°.

N-Phenylbenzimino-*o*-chlorophenyl ether and *N*-phenylbenzimino-*p*-chlorophenyl ether, heated at 270—290° for 2 hours, gave benzoyl-*o*- and -*p*-chlorodiphenylamine, respectively, by changes corresponding to that of (I) into (II).

The mobile group must therefore have become attached to the nitrogen atom by the nuclear carbon atom originally attached to the oxygen (compare Montagne, *Ber.*, 1918, **51**, 1479).

The assumption has frequently been made that in changes of this character the migration of the mobile atom or group is preceded by its partial dissociation from the remainder of the molecule, followed by a redistribution of the valency bonds and recombination to form the isomeric compound; some workers have assumed complete dissociation (Brühl, *Ber.*, 1899, **32**, 2326; Lapworth, J., 1901, **79**, 1265; Nef, *J. Amer. Chem. Soc.*, 1904, **26**, 1549). The absence of by-products formed by the combination of two similar free radicals could be accounted for by regarding the dissociation as ionic in character. Recently Meerwein and van Emster (*Ber.*, 1922, **55**, 2500; compare also *Annalen*, 1923, **435**, 190, 207) have applied this view to the interpretation of the isomeric change of camphene hydrochloride into bornyl chloride, and have shown that the velocities of the transformation in different solvents are proportional to the ionising powers of the latter. Others, however, have preferred to express the course of such transformations in terms of partial valencies without assuming the formation of ions or free radicals (Robinson, *Mem. Manc. Lit. Phil. Soc.*, 1920, **64**, No. 4; Tiffeneau, *Rev. Gen. Sci.*, 1907, 583; Stark, "Prinzipien der Atomdynamik," 1915, III, 156; Mumm, Hesse, and Volquartz, *loc. cit.*).

It seemed desirable to test the validity of the ionic hypothesis in the present instance, and a number of measurements were made of the electrical conductivity of the imino-ether and its isomeride before, during, and after the completion of the isomeric change. The results obtained were mainly comparative. The specific conductivity of the imino-ether between 250° and 280° was of the order 10^{-8} to 10^{-9}. The low conductivity of the imino-ether remained constant so long as no appreciable isomeric change occurred, as was shown by heating the ether at 200° for several hours. When the imino-ether was heated at a higher temperature, an increase in conductivity occurred simultaneously with the isomeric change. At first rapid, it became slower, and finally the conductivity remained constant, the end of the increase coinciding with the completion of the isomeric change. Samples of benzoyldiphenylamine had identical conductivities within the range of experimental error whether prepared (*a*) by heating the imino-ether, or (*b*) as in (*a*) but subsequently crystallised from alcohol and dried, or (*c*) from diphenylamine and benzoyl chloride. The specific conductivity was of the order of 10^{-6} to 10^{-7} at 250—280°.

These observations can readily be explained in terms of the ionic hypothesis by supposing that the first stage consists in the rupture of the bond between the phenyl radical and the oxygen atom, a phenyl ion and an ionised residue being produced; re-

arrangement of the linkings in the residue follows, and combination of the phenyl ion with the nitrogen atom :

$$PhC\langle^{NPh}_{OPh} \longrightarrow PhC\langle^{NPh}_{O\cdots} + Ph\cdots \longrightarrow$$

$$PhC\langle^{NPh\cdots}_{O} + Ph\cdots \rightleftharpoons PhC\langle^{NPh_2}_{O}.$$

The first stage would give the reaction its unimolecular character, the succeeding ones being comparatively very rapid. The final stage would result in an equilibrium between ionised and non-ionised benzoyldiphenylamine.

The results of the determinations with different samples of benzoyldiphenylamine rendered it unlikely that the observed conductivity change was due to a trace of a by-product formed during the transformation; but the possibility was not excluded that it might arise from the constant presence of a trace of impurity in the changing medium of the molten mixture. Such a source of error—which might arise from the liberation of water adsorbed on the glass walls of the cell, as well as from the presence of impurities in the substances used—could be guarded against only partially by careful purification of material and apparatus, and hence it was decided to employ a more trustworthy test of the ionisation of the materials undergoing change.

N-*p*-Tolylbenzimino-*p*-tolyl ether undergoes rearrangement at the same temperatures as *N*-phenylbenziminophenyl ether. If the change is ionic in the one case, it should be so in the other, and if a mixture of these two imino-ethers were heated at the transformation temperature a certain amount of benzoylphenyl-*p*-tolylamine should be formed by exchange of the mobile groups, in addition to the two symmetrical products.

$$PhC(:NPh)\cdot OPh \longrightarrow PhCO\cdot NPh\cdots + Ph\cdots \rightleftharpoons PhCO\cdot NPh_2$$

$$\rightleftharpoons PhCO\cdot NPh(C_7H_7)$$

$$PhC(:N\cdot C_7H_7)\cdot O\cdot C_7H_7 \rightarrow PhCO\cdot N\cdot C_7H_7\cdots + C_7H_7\cdots \rightleftharpoons$$

$$PhCO\cdot N(C_7H_7)_2$$

A mixture of *N*-phenylbenziminophenyl ether and *N*-*p*-tolylbenzimino-*p*-tolyl ether in equal molecular proportions was heated at 290° until the freezing point of the product was constant (139·8°). This freezing point was identical with that of a freshly made mixture of benzoyldiphenylamine and benzoyldi-*p*-tolylamine in equal molecular proportions. After the latter mixture had been heated for several hours at 250—290°, the freezing point was unchanged, showing that here again no third substance was produced. Inter-

change of groups to form benzoylphenyl-*p*-tolylamine had therefore not taken place.

The conclusion cannot be resisted, in view of this evidence, that the isomeric change of an imino-ether into a substituted amide is not ionic in character. This conclusion can probably be extended to other isomeric changes, where, under the influence of heat, an aryl group migrates to a different position in the molecule, and serves to confirm the view, recently expressed (*Ann. Rep.*, 1924, 98), that the ionic hypothesis should be applied only to those structures which exhibit independent evidence of capacity to ionise.

Experimental.

Preparation and Purification of Materials.—The *N*-phenylbenziminophenyl ether was prepared by the same method as *N*-phenylbenzimino-*m*-hydroxyphenyl ether (J., 1922, **121**, 1679). It was recrystallised from alcohol until both the m. p. (105°) and the velocity of isomeric change were constant. Further recrystallisation from benzene produced no effect on either property.

The benzoyldiphenylamine prepared from diphenylamine and benzoyl chloride was recrystallised from alcohol until the m. p. was constant.

Dynamical Experiments.—Five grams of imino-ether were used for each determination. The material, in a test-tube, was rapidly heated to approximately the required temperature in a separate oil-bath and then quickly transferred to an electrically heated, oil-filled thermostat maintained within 0·5° of the temperature of the experiment. At the end of the required time the tube was removed; the cooled melt could then be analysed at leisure.

The freezing-point determinations were conducted in the same tube, which was enclosed in a wider tube, itself immersed in an oil-bath maintained a few degrees below the freezing point of the mixture. Readings were easily obtained concordant to 0·25°, corresponding to an accuracy of 0·5%.

The freedom of the benzoyldiphenylamine from impurity when obtained by prolonged heating of the imino-ether (10 g., heated at 280° for 3 hours and then at 290° for 50 minutes) was proved by the identity of its freezing point with that of pure benzoyldiphenylamine (176·7°). A special thermometer was used which could be read to 0·05°.

Isomeric Change of Chloro-substituted Imino-ethers.—These compounds were prepared from *o*- and *p*-chlorophenols by the method referred to above.

N-*Phenylbenzimino*-o-*chlorophenyl ether* crystallises from alcohol in almost colourless, stout prisms, m. p. 88°. It is very soluble in hot

alcohol, but only sparingly soluble in cold (Found: N, 4·6. $C_{19}H_{14}ONCl$ requires N, 4·55%).

When heated at 270—280° for 1 hour and then crystallised from alcohol, it yielded hard crusts of constant m. p. 95—96°, which did not depress the m. p. of benzoyl-*o*-chlorodiphenylamine prepared as described below (Found: N, 4·7. $C_{19}H_{14}ONCl$ requires N, 4·55%).

N-*Phenylbenzimino*-p-*chlorophenyl ether* crystallised from alcohol in pale yellow, long prisms, m. p. 92—93° (Found: N, 4·75%). Hydrolysis with 50% sulphuric acid yielded *p*-chlorophenyl benzoate (m. p. 88—88·5°) identical with a sample prepared from *p*-chlorophenol. When heated at 280—290° for 2 hours and then recrystallised from alcohol, it yielded long prisms of constant m. p. 109—110° which did not depress the m. p. of benzoyl-*p*-chlorodiphenylamine prepared as described below (Found: N, 4·7%).

Benzoyl-o-, -m-, and -p-*chlorodiphenylamines* were prepared as described by Ullmann (*Annalen*, 1907, **355**, 338) by heating the corresponding chlorophenylanthranilic acids. o-*Chlorodiphenylamine* was obtained only after heating *o*-chlorophenylanthranilic acid at 300—320° for 5 hours. It is a pale yellow oil, b. p. 300—303°/753 mm.

The bases were benzoylated by heating with benzoyl chloride, and the benzoyl derivatives crystallised from alcohol.

Benzoyl-o-*chlorodiphenylamine*, m. p. 95° (Found: N, 4·6%), and *benzoyl*-m-*chlorodiphenylamine*, m. p. 101—102° (Found: N, 4·6%), crystallise in hard crusts; the m. p. of the latter was depressed by the addition of either of the substances prepared by heating the *o*- and *p*-chloro-iminoethers. *Benzoyl*-p-*chlorodiphenylamine* crystallises in prisms, m. p. 109—109·5° (Found: N, 4·7%).

Measurements of Electrical Conductivity.—The electrodes were bright platinum foil cylinders 1·0 and 0·7 cm. respectively in diameter and 1 cm. high, secured in position one inside the other by sealing their platinum stems through two rigidly connected glass tubes. The constant of the cell was approximately $2·4 \times 10^{-2}$ at 21°, and no appreciable leak could be detected at 275°.

As the resistances to be measured were very high (10^5 to 10^7 ohms), the arrangement devised by Ambronn (*Ann. Physik*, 1919, **58**, 139) was employed, consisting of a battery and galvanometer connected to the conductivity cell through a rotating commutator which reversed the current through the cell about 100 times per second. The apparatus was calibrated by comparison with a series of standard high resistances.

The samples (5 g. in each case) were well dried and heated as in the dynamical experiments. The electrodes were immersed in the

fused material, and readings taken from time to time throughout the whole period of the transformation. The temperatures employed varied from 260° to 280°.

N-p-*Tolylbenzimino*-p-*tolyl ether*, prepared from benz-*p*-toluidide-iminochloride and *p*-cresol by the method already described, formed very pale yellow prisms, m. p. 65—66° (Found : N, 4·75. $C_{21}H_{19}ON$ requires N, 4·65%). When heated at 270—300° for 2 hours, it yielded *benzoyldi*-p-*tolylamine ;* this, prepared also from di-*p*-tolylamine and benzoyl chloride, formed nearly colourless prisms, m. p. 124—125° (Found : N, 4·7. $C_{21}H_{19}ON$ requires N, 4·65%).

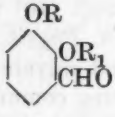
The author wishes to express his indebtedness to the Chemical Society for a grant which has defrayed part of the expenses of this investigation, and to Messrs. Metropolitan-Vickers Electrical Company, Ltd., for the loan of the rotating commutator.

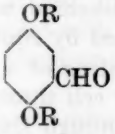
THE UNIVERSITY, SHEFFIELD. [*Received, June 20th*, 1925.]

CCLXX.—*Substitution in Derivatives of Quinol Ethers.*

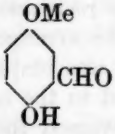
By LEON RUBENSTEIN.

THE investigation of substitution in the case of dialkyloxy vicinal benzene derivatives of type I (Davies and Rubenstein, J., 1923, **123**, 2830) showed that during nitration each alkyloxy-group OR,OR_1 exerts its para-directing influence independently of the other, whereas during bromination only the group –OR is potent in determining the orientation of the brominated product. The relative amounts of the isomerides produced in the nitration experiments, which could not then be estimated, have now been determined in the case of *o*-veratraldehyde (Perkin, Robinson, and Stoyle, J., 1924, **125**, 2355). The results obtained in those investigations made it desirable to examine the nitration and bromination of substances of type II in which only ortho-substitution with respect to the alkyloxy-groups can take place.

(I.) 



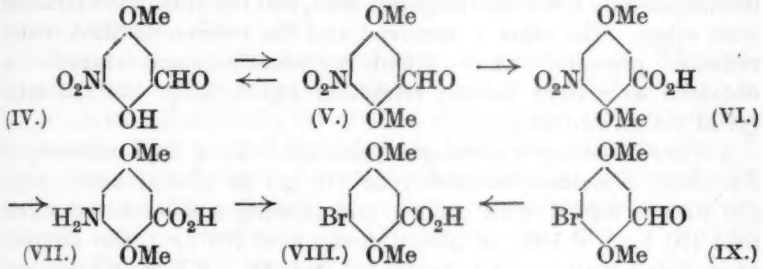
(II.)



(III.)

Experiments on the nitration of 2-hydroxy-5-methoxybenzaldehyde (III) indicate that the substance formed is the 3-nitro-benzaldehyde (IV), for when its methylation product (V) is hydrolysed 3-*nitro*-2-*hydroxy*-5-*methoxybenzaldehyde* is reformed. The bromin-

ation of 2-hydroxy-5-methoxybenzaldehyde yields the 3-bromobenzaldehyde, as is shown in the following manner: 3-*Nitro*-2 : 5-*dimethoxybenzaldehyde* (V) is oxidised to 3-*nitro*-2 : 5-*dimethoxybenzoic acid* (VI), which is reduced to 3-*amino*-2 : 5-*dimethoxybenzoic acid* (VII); from this by the Sandmeyer process is produced 3-*bromo*-2 : 5-*dimethoxybenzoic acid* (VIII), identical with the acid obtained by oxidising bromo-2-hydroxy-5-methoxybenzaldehyde after methylation (IX).



The nitration of 2 : 5-dimethoxybenzaldehyde gives a mixture of 6-*nitro*-2 : 5-*dimethoxybenzaldehyde* (80%) and 3-*nitro*-2 : 5-*dimethoxybenzaldehyde* (20%). The former substance has its nitro-group in the ortho-position with respect to the aldehyde group, for it gives an indigotin derivative when treated with acetone and alkali. It yields 6-nitro-2 : 5-dimethoxybenzoic acid on oxidation. The bromination of 2 : 5-dimethoxybenzaldehyde gives 6-*bromo*-2 : 5-*dimethoxybenzaldehyde* as the only product, and from this 6-*bromo*-2 : 5-*dimethoxybenzoic acid* is obtained by oxidation.

The remaining portion of the work consists in the investigation of the nitration and the bromination of 2 : 5-dimethoxyacetanilide. The nitration of this substance yields 4-*nitro*-2 : 5-*dimethoxyacetanilide*, as is shown by the fact that hydrolysis converts it into the nitro-2 : 5-dimethoxyaniline which on diazotisation and subsequent treatment in the Sandmeyer manner yields 3-*bromo*-6-*nitroquinol dimethyl ether*. On bromination, 2 : 5-dimethoxyacetanilide yields 4-*bromo*-2 : 5-*dimethoxyacetanilide*, the usual proof being applied, namely, conversion into the 4-*bromo*-2 : 5-*dimethoxyaniline*, diazotisation, and treatment with cuprous bromide to give dibromoquinol dimethyl ether.

EXPERIMENTAL.

2-Hydroxy-5-methoxybenzaldehyde was obtained by Tiemann and Müller (*Ber.*, 1881, **14**, 1990) in small yield, but the following modification gives much better results. Quinol monomethyl ether (40 g.) dissolved in a concentrated aqueous solution of sodium hydroxide (19 g. in 55 c.c. of water) is heated on a water-bath

while chloroform (42 g.) and sodium hydroxide solution (56 g. in 60 c.c. of water) are added alternately during 2 hours. The mixture is then heated for 1 hour, the sodium salt of the aldehyde separating in yellow, metallic crystals. The whole is strongly acidified, steam-distilled, the distillate extracted with ether, and the ethereal extract kept for some time over a concentrated solution of sodium bisulphite. The major portion of the ether is distilled off and the bisulphite compound of the aldehyde, which separates, is removed, decomposed by hot dilute sulphuric acid, and the aldehyde extracted with ether. The ether is removed and the residue distilled under reduced pressure, when 2-hydroxy-5-methoxybenzaldehyde is obtained as a light yellow, refracting liquid, b. p. 124°/12 mm. (yield 8·5 g., *i.e.*, 25%).

3-*Nitro*-2-*hydroxy*-5-*methoxybenzaldehyde*.—To a cold solution of 2-hydroxy-5-methoxybenzaldehyde (10 g.) in glacial acetic acid (50 c.c.) is added with cooling and stirring a solution of nitric acid (50 c.c.; *d* 1·42) in glacial acetic acid (50 c.c.), the temperature being maintained between 10° and 20°. 3-Nitro-2-hydroxy-5-methoxybenzaldehyde, which soon begins to separate, is collected after a few hours (yield 6·5 g.; m. p. 127°). The glacial acetic acid solution is diluted with water, neutralised with sodium bicarbonate, and extracted with ether; from the extract a further 4·5 g. of the substance is obtained (total yield 88%). 3-Nitro-2-hydroxy-5-methoxybenzaldehyde crystallises in bright yellow needles, m. p. 132°. It does not yield an indigotin derivative when treated with acetone and sodium hydroxide solution. With ferric chloride solution, it gives a red coloration (Found: N, 7·2. $C_8H_7O_5N$ requires N, 7·1%).

The p-*nitrophenylhydrazone* crystallises in scarlet prisms, decomp. 250°.

3-*Nitro*-2 : 5-*dimethoxybenzaldehyde*.—A solution of 3-nitro-2-hydroxy-5-methoxybenzaldehyde (6 g.) in dry chloroform (20 c.c.) and methyl iodide (10 c.c.) is heated on a water-bath while finely powdered silver oxide (6 g.) is added during 2 hours. After being heated for a further 1 hour, the mixture is filtered hot, some of the chloroform evaporated, and the solution cooled; 3-nitro-2 : 5-dimethoxybenzaldehyde then crystallises in pale yellow needles, m. p. 113°. More of the substance is obtained from the mother-liquors (yield almost theoretical) (Found: N, 6·85. $C_9H_9O_5N$ requires N, 6·7%). When it is boiled for a short time with 10% sodium hydroxide, and the solution is acidified, 3-nitro-2-hydroxy-5-methoxybenzaldehyde can be extracted from the precipitate obtained.

3-*Bromo*-2-*hydroxy*-5-*methoxybenzaldehyde*.—2-Hydroxy-5-meth-

oxybenzaldehyde (6 g.) is dissolved in glacial acetic acid (30 c.c.), and powdered, freshly-fused sodium acetate (3·6 g.) added. The suspension is well stirred, cooled to 5°, and treated with a solution of bromine (6 g.) in glacial acetic acid (12 c.c.), when 3-*bromo*-2-*hydroxy*-5-*methoxybenzaldehyde* rapidly separates. After remaining for a few hours, the mixture is diluted with water and the solid collected (yield 7·3 g. or 80%). It crystallises from aqueous alcohol in light brown needles, m. p. 107° (Found: Br, 35·0. $C_8H_7O_3Br$ requires Br, 34·6%). The p-*nitrophenylhydrazone* forms scarlet prisms, decomp. above 250°.

3-*Bromo*-2 : 5-*dimethoxybenzaldehyde*.—A solution of 3-bromo-2-hydroxy-5-methoxybenzaldehyde (6·5 g.) in alcohol (59 c.c.) is boiled under reflux during the gradual addition of methyl *p*-toluenesulphonate (10·5 g.) and 30% sodium hydroxide solution (4 c.c.). After boiling for 3 hours, the red alcoholic solution is diluted with water and the solid collected; after twice crystallising from aqueous alcohol, it forms needles, m. p. 63° (Found: Br, 32·3. $C_9H_9O_3Br$ requires Br, 32·6%).

Nitration of 2 : 5-*Dimethoxybenzaldehyde*.—Finely-powdered 2 : 5-dimethoxybenzaldehyde (3 g.) was added with cooling and stirring to cold nitric acid (12 c.c.; *d* 1·42). After remaining at room temperature for several hours, the mixture was diluted with water, and the solid (3·4 g.) collected. The mixture, m. p. 130—153°, was fractionally crystallised from alcohol, the main product being 6-*nitro*-2 : 5-*dimethoxybenzaldehyde* (*vide ante*), m. p. 159°. The mother-liquors deposited a small amount of 3-*nitro*-2 : 5-*dimethoxybenzaldehyde* (m. p. 113°), which gave no depression of melting point when mixed with a sample of 3-nitro-2 : 5-dimethoxybenzaldehyde prepared by the methylation of 3-nitro-2-hydroxy-5-methoxybenzaldehyde (p. 2000).

6-Nitro-2 : 5-dimethoxybenzaldehyde crystallises from alcohol in pale yellow needles, m. p. 159° (Found: N, 6·8. $C_9H_9O_5N$ requires N, 6·7%). The p-*nitrophenylhydrazone* forms scarlet prisms, m. p. 245—250° (decomp.).

6-*Bromo*-2 : 5-*dimethoxybenzaldehyde*.—A cooled solution of 2 : 5-dimethoxybenzaldehyde (2·8 g.) in glacial acetic acid (16 c.c.) is treated with bromine (2·8 g.) in glacial acetic acid (8 c.c.), kept for 2 days, and diluted with water; an oil then separates which rapidly solidifies. It crystallises from alcohol in pale grey needles, m. p. 125—126°, which become pink on exposure to the air (Found: Br, 29·1. $C_9H_9O_3Br$ requires Br, 28·7%). The p-*nitrophenylhydrazone* consists of hexagonal, scarlet prisms, m. p. 204—206°.

3-*Nitro*-2 : 5-*dimethoxybenzoic Acid*.—3-Nitro-2 : 5-dimethoxybenzaldehyde (6 g.) is added to water (60 c.c.) containing potassium

bicarbonate (4·2 g.), and boiled during the addition of potassium permanganate solution (6 g. in 60 c.c. of water). The hot solution is filtered, allowed to cool, and unchanged aldehyde collected. The reddish-yellow aqueous solution is acidified with dilute hydrochloric acid, when 3-nitro-2 : 5-dimethoxybenzoic acid (3·5 g.) is precipitated. It crystallises from hot water in long needles, m. p. 182—183° (Equiv. : found, 225; calc., 227).

6-*Nitro*-2 : 5-*dimethoxybenzoic Acid.* — 6-Nitro-2 : 5-dimethoxybenzaldehyde is oxidised as described above. The acid crystallises from hot water in pale yellow prisms, m. p. 192° (Equiv. : found, 229; calc., 227).

3-*Amino*-2 : 5-*dimethoxybenzoic Acid.*—A mixture of 3-nitro-2 : 5-dimethoxybenzoic acid (7 g.) and concentrated hydrochloric acid (24 c.c.) is gradually treated with tin (7 g.) and heated on a water-bath for 3 hours, water (50 c.c.) is added, and the tin removed from the hot solution as sulphide. The colourless filtrate is evaporated under reduced pressure, when the *hydrochloride* of 3-*amino*-2 : 5-*dimethoxybenzoic acid* separates in long, white needles (yield 5 g. or 80%).

The hydrochloride is easily soluble in water or alcohol, more difficultly soluble in concentrated hydrochloric acid, from which it can be crystallised. The solutions turn pink and then red on exposure to the air. When heated, the solid becomes very dark at 170° and decomposes at 215°. 3-*Amino*-2 : 5-*dimethoxybenzoic acid* is obtained by treating a solution of the hydrochloride in a small quantity of water with solid sodium carbonate until it is just acid to Congo-red, and evaporating under reduced pressure; after a long time, the acid separates in white, slender needles which turn black at 170° and decompose at 210—215°. It is soluble in acids, alkalis, and hot water; the latter two solutions turn green on exposure to the air (Found : N, 6·9. $C_9H_{12}O_4N$ requires N, 7·0%).

3-*Bromo*-2 : 5-*dimethoxybenzoic Acid.*—A mixture of 3-bromo-2 : 5-dimethoxybenzaldehyde (5·5 g.), water (55 c.c.), and potassium bicarbonate (3·8 g.) is boiled during the addition of 10% potassium permanganate (55 c.c.), filtered hot, cooled, and again filtered. The colourless filtrate is acidified with dilute hydrochloric acid, and the precipitated 3-*bromo*-2 : 5-*dimethoxybenzoic acid* (yield 4·5 g. or 85%) is crystallised from aqueous alcohol, when it is obtained in white, microscopic prisms, m. p. 132° (Equiv. : found, 258; calc., 261).

6-*Bromo*-2 : 5-*dimethoxybenzoic Acid.*—6-Bromo-2 : 5-dimethoxybenzaldehyde is oxidised as described above. The acid crystallises from aqueous alcohol in white, microscopic prisms, m. p. 164—165° (Equiv. : found, 259; calc., 261).

4 : 4′ : 7 : 7′-Tetramethoxyindigotin.—Aqueous potash (1 c.c. of 10%) is added to a solution of 6-nitro-2 : 5-dimethoxybenzaldehyde (0·4 g.) in acetone (2 c.c.). The deep blue liquid is mixed with water (20 c.c.) and boiled for a few minutes; the indigotin then separates. It has a rich deep blue appearance and crystallises from nitrobenzene in deep purple rhombs which sublime at 350°.

4-Bromo-2 : 5-dimethoxyacetanilide.—When 2 : 5-dimethoxyacetanilide (5 g.) dissolved in glacial acetic acid (25 c.c.) is treated with bromine (3·3 g.) in 4 c.c. of glacial acetic acid, *4-bromo-2 : 5-dimethoxyacetanilide* soon separates from the well-cooled solution. After the mixture has been diluted with water, and the acetic acid neutralised with sodium carbonate, ether extracts the product, which crystallises from dilute alcohol in pale pink rhombs, m. p. 122° (yield 5·6 g. or 80%) (Found: Br, 29·3. $C_{10}H_{12}O_3NBr$ requires Br, 29·1%).

4-Bromo-2 : 5-dimethoxyaniline Hydrochloride.—4-Bromo-2 : 5-dimethoxyacetanilide (12 g.) is boiled with 20% alcoholic hydrochloric acid (20 c.c.) for 15 minutes; the *4-bromo-2 : 5-dimethoxyaniline hydrochloride* which separates crystallises from alcohol in white, microscopic plates which become blue at 160° and decompose above 300°.

4-Bromo-2 : 5-dimethoxyaniline forms pale pink prisms, m. p. 106°. The *hydrobromide* is obtained by keeping an ethereal solution of the base in contact with hydrobromic acid (*d* 1·5), when it slowly separates in fine, yellow needles which turn blue at 160° and decompose slowly above this temperature.

Diazotisation. Methyl nitrite is passed through a solution of 4-bromo-2 : 5-dimethoxyaniline hydrobromide (20 g.) in glacial acetic acid (60 c.c.) at 10°. The deep brown solution of 4-bromo-2 : 5-dimethoxybenzenediazonium bromide is poured into dry ether, the ether decanted off, and the solid diazonium salt dissolved in ice-cold water (40 c.c.). The aqueous solution is added cautiously to a solution of cuprous bromide in concentrated hydrobromic acid and heated on a water-bath; nitrogen is then evolved and 2 : 5-dibromoquinol dimethyl ether separates. This crystallises from alcohol in colourless needles, m. p. 143°, not depressed on admixture with the dibromoquinol dimethyl ether prepared by the bromination of quinol dimethyl ether.

4-Nitro-2 : 5-dimethoxyacetanilide.—A solution of 2 : 5-dimethoxyacetanilide (10 g.) in glacial acetic acid (50 c.c.) is treated at 5° with nitric acid (*d* 1·42; 10 c.c. in 50 c.c. of glacial acetic acid). After 1 hour, water is added. The *4-nitro-2 : 5-dimethoxyacetanilide* which separates (yield 11 g. or 90%) crystallises from alcohol in yellow prisms, m. p. 165° (Found: N, 11·8. $C_{10}H_{12}O_5N_2$ requires N, 11·7%).

4-Nitro-2 : 5-dimethoxyaniline Hydrochloride.—4-Nitro-2 : 5-dimethoxyacetanilide (10 g.) is boiled with 20% alcoholic hydrochloric acid (25 c.c.) for 1 hour. The grey crystals of the *hydrochloride* that separate on cooling (yield theoretical) crystallise from alcohol in yellow, metallic prisms, m. p. 160° (decomp.) (Found: N, 12·1. $C_8H_{11}O_4N_2Cl$ requires N, 11·9%).

4-Nitro-2 : 5-dimethoxyaniline forms yellow prisms, m. p. 153°.

Diazotisation of 4-Nitro-2 : 5-dimethoxyaniline Hydrobromide.—The solution obtained by diazotising 4-nitro-2 : 5-dimethoxyaniline hydrobromide (4 g.) in concentrated hydrobromic acid (20 c.c.) and water (25 c.c.) at 0° with 2·5 c.c. of 40% sodium nitrite is filtered, added cautiously to a solution of cuprous bromide in concentrated hydrobromic acid, and the mixture heated on a water-bath for a short time. The 2-bromo-5-nitroquinol dimethyl ether that separates is washed with concentrated hydrobromic acid and with water and crystallised from alcohol. The product, pale yellow prisms, m. p. 154°, does not depress the m. p. of 2-bromo-5-nitroquinol dimethyl ether obtained by bromination of nitroquinol dimethyl ether.

The author is indebted to the Research Fund Committee of the Chemical Society for a grant which has defrayed some of the expenses of this investigation.

THE DYSON PERRINS LABORATORY,
OXFORD. [*Received, June 30th,* 1925.]

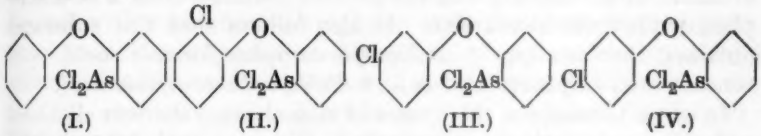
CCLXXI.—*The Relative Rates of Conversion of Phenoxyphenyldichloroarsine and its Chloro-derivatives into Chlorophenoxarsines.*

By ELWYN ROBERTS and EUSTACE EBENEZER TURNER.

IT was previously shown (Turner and Sheppard, this vol., p. 544) that *o*-phenoxyphenyldichloroarsine readily passes into 5-chlorophenoxarsine (there named 6-chlorophenoxarsine) when distilled under diminished pressure, and it was suggested that polarity effects might account for this then unusual ring-closure. It was therefore decided to test the effect, on the ring-closure, of a polar substituent in the dichloroarsine. In starting the work, the present authors were unaware of the fact that diphenylyl-*o*-arsenious chloride is readily converted into *oo'*-diphenylylenearsenious chloride (Aeschlimann, Lees, McCleland, and Nicklin, this vol., p. 66).

It having been found that *o*-phenoxyphenyldichloroarsine under-

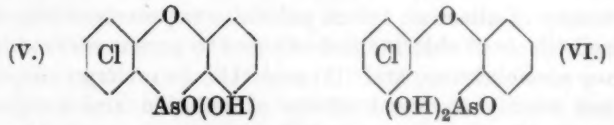
went ring-closure at a readily measurable rate when heated at 200° in a current of carbon dioxide, it was decided to compare, under these conditions, the rate of ring-closure of the parent *o*-phenoxy-compound (I) and its *ortho*- (II), *meta*- (III), and *para*- (IV) chloro-derivatives :



(I.) (II.) (III.) (IV.)

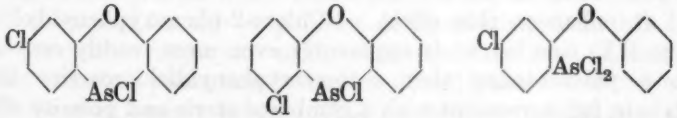
Compounds (II), (III) and (IV) were synthesised from the appropriate chlorophenol by processes similar to that originally used for the synthesis of (I). Preliminary experiments showed that whilst the compounds (II) and (IV) could be distilled under diminished pressure with only partial decomposition, compound (III) underwent very considerable ring-closure, a result which at first sight appeared to support the alternate polarities theory.

5 : 8- (see below) and 5 : 7-*Dichlorophenoxarsines* were prepared in two ways; first, by prolonged boiling of dichloroarsines (III) and (IV) under diminished pressure, and secondly by the reduction (hydrochloric–hydriodic–sulphurous acid method) of the corresponding chlorophenoxarsinic acids (V), the latter being obtained by the action of warm concentrated sulphuric acid on the corresponding chlorophenoxyphenylarsinic acids (VI) :



5 : 9-*Dichlorophenoxarsine* was prepared by boiling the corresponding phenoxydichloroarsine under diminished pressure.

The constitutions of three of the chlorophenoxarsines follow from their mode of formation from the corresponding dichloroarsines. That of the chlorophenoxarsine obtained from 2-m-*chlorophenoxyphenyldichloroarsine*, however, may be either (VII) or (VIII) :



(VII.) (VIII.) (IX.)

5 : 8-Dichlorophenoxarsine (VII) has therefore been synthesised by a process which leaves no doubt as to its constitution. When 2 : 4-dichloronitrobenzene is warmed with 1 mol. of potassium phenoxide in phenol as solvent, the 2-chlorine atom is displaced by

phenoxyl. The resulting *5-chloro-2-nitrodiphenyl ether* is readily converted by the usual series of reactions into *4-chloro-2-phenoxyphenyldichloroarsine* (IX), and the latter, when heated at 200° in a current of carbon dioxide affords 5 : 8-dichlorophenoxarsine, identical in all respects with the product obtained from 2-*m*-chlorophenoxyphenyldichloroarsine. It also follows that the substance obtained by heating 2-m-*chlorophenoxyphenylarsinic acid* with concentrated sulphuric acid is 5 : 8-*dichlorophenoxarsinic acid*.

In order to compare their rates of ring-closure, the four dichloroarsines were heated simultaneously in the same bath kept at 200°. Through each dichloroarsine carbon dioxide was bubbled at the same rate, and the hydrogen chloride liberated was determined at intervals. In this way it was found (see p. 2012) that *o*-phenoxyphenyldichloroarsine (I) undergoes ring-closure much more readily than does its *m*-chloro-derivative (III), whilst the latter in turn undergoes ring-closure much more rapidly than the ortho- (II) or para- (IV) derivative, the last two compounds undergoing ring-closure at approximately equal rates.

This result appears to show conclusively that the polarising effect of the chlorine atom is not the sole determining influence affecting ring-closures of dichloroarsines to chlorophenoxarsines, just as the polarising effect of the oxygen atom can no longer be regarded as the main determining influence causing the ready formation of 5-chlorophenoxarsine itself.

The theory of alternate latent polarities requires compound (III) (combined effects of chlorine and oxygen) to pass more readily than (I) into a phenoxarsine, and (II) and (IV) to undergo ring-closure much less readily (opposed effects of chlorine and oxygen). A purely steric effect on the part of the chlorine atom would account for the observed fact that compound (I) undergoes ring-closure more readily than compound (III), but scarcely explains why (II) and (IV) pass into chlorophenoxarsines so much less readily. The main determining factor appears to be a steric one, modified by polar effects. In the case of compound (III), the steric outweighs the polar effect of the chlorine atom, whilst in the case of (II) and (IV) it enhances this effect. 4-Chloro-2-phenoxyphenyldichloroarsine (IX) (see below) is apparently even more readily converted into a phenoxarsine than *o*-phenoxyphenyldichloroarsine itself. This is in full agreement with a combined steric and polarity effect. In explaining the results obtained, Flürscheim's theory does not appear to present any advantages over the theory of alternate latent polarities, which, on this occasion at any rate, seems to be capable of definite interpretation, whilst the more subtle alternation of free affinity is not readily dealt with in the case of two key-atoms

having opposite effects. The observations of Altschul in connexion with the coupling of diazo-solutions with the isomeric nitrophenols are of interest in comparison with the present results (*Chem.-Ztg.*, 1898, **22**, 115).

When *o*-phenoxy- or 2-*o*-chlorophenoxy-phenylarsinic acid is heated with concentrated sulphuric acid, the corresponding phenoxarsinic acid is not obtained. Since each phenyl nucleus in diphenyl ether is readily monosulphonated, the different behaviour of the four phenoxyphenylarsinic acids may be explained as follows: Phenoxyphenylarsinic acid itself readily undergoes sulphonation in the unsubstituted phenyl nucleus, so that the final product is a sulphonic acid of the simple arsinic acid or of the phenoxarsinic acid. 2-*o*-Chlorophenoxyphenylarsinic acid, owing to combined polar and steric effects of the chlorine atom, undergoes sulphonation more rapidly than ring-closure. 2-*m*-Chlorophenoxyphenylarsinic acid shows a greater tendency to undergo ring-closure than to sulphonate, owing to the steric effect, on sulphonation, of the chlorine atom, whilst 2-*p*-chlorophenoxyphenylarsinic acid is readily converted into a phenoxarsinic acid, owing to the presence of a chlorine atom in the position at which sulphonation would occur.

The mechanism of the hydrochloric–hydriodic–sulphurous acid reduction of arsinic acids to dichloroarsines is imperfectly understood. In the reduction of 4-chloro-2-phenoxyphenylarsinic acid, free iodine is liberated as reduction proceeds, and appears as a surface film, which, although readily broken up by agitation, continually reappears, whilst any arsinic acid remains unreduced. Suddenly the oily dichloroarsine–oxychloride–acid mixture solidifies, owing to its conversion into dichloroarsine, and at once the iodine film disappears. Similar, although less definite, changes occur in other cases, and it would therefore appear clear that hydriodic acid is the essential reducing agent, being immediately oxidised in presence of even small quantities of an arsinic acid.

Experimental.

Preparation of 2-, 3-, *and* 4-*Chloro-2'-nitrodiphenyl Ethers.*—The method adopted for the preparation of these compounds has been that previously employed, using *o*-chloronitrobenzene (1 mol.), a phenol (2 mols.), potassium hydroxide (1 mol.), and water (0·3 mol.) in presence of copper bronze. The yields given below are calculated on the chloronitrobenzene. If the proportion of alkali be increased (say, to 1·5 mols.), unworkable tars result, but in the case of the condensation with *m*-chlorophenol, a substance only obtainable with difficulty, the proportion of phenol may be reduced to 1 mol. without seriously decreasing the yield.

2-*Chloro*-2′-*nitrodiphenyl ether* was obtained in 55% yield, forms yellow, hexagonal prisms or plates from alcohol, and has m.p. 48°, b. p. 209°/9 mm. (Found: NO_2, 18·8. $C_{12}H_8O_3NCl$ requires NO_2, 18·4%).

3-*Chloro*-2′-*nitrodiphenyl ether*, obtained in 58% yield, is a yellow oil, b. p. 204°/8 mm. [Found (crude substance) NO_2, 17·3%]. The *m*-chlorophenol required was obtained by Hodgson's method (*Brit. Pat.* 200714) from *m*-chloroaniline. The addition of copper sulphate to the diazo-solution appears to improve the yield (94%) slightly. The *m*-chloroaniline used was readily prepared in almost theoretical yield by reducing *m*-chloronitrobenzene by the iron–ferric chloride method (below).

4-*Chloro*-2′-*nitrodiphenyl ether*, obtained in 75% yield, separates from alcohol in yellow needles, m. p. 44—45°, b. p. 208°/11 mm., or 220°/20 mm. (Found: Cl, 14·7; NO_2, 18·9. $C_{12}H_8O_3NCl$ requires Cl, 14·2; NO_2, 18·4%).

Preparation of Aminodiphenyl Ethers.—The method previously adopted for the reduction of nitrodiphenyl ethers has been abandoned in favour of the following, which gives excellent yields. A mixture of nitro-compound (1 part), iron filings (1·5 parts), and water (1 part) was heated for about 10 minutes in boiling water, with thorough shaking. A gram of ferric chloride for each 100 g. of iron was then added and the whole shaken and heated until a reaction set in. The reaction was controlled if necessary by removal from the bath, and finally completed by heating in boiling water for an hour. The cooled product was shaken with ether, filtered, and the iron residue washed with ether. The ethereal solution was shaken with an excess of hydrochloric acid, when the base separated as the hydrochloride. The iron residues become warm on exposure to air, owing to rapid oxidation.

All the amino-compounds are stable, and distil unchanged in a vacuum.

o-*Aminodiphenyl ether*, obtained in almost theoretical yield, forms an *acetyl* derivative, colourless prisms from light petroleum (b. p. 80—100°) (Found: N, 6·4. $C_{14}H_{13}O_2N$ requires N, 6·2%).

2-*Chloro*-2′-*aminodiphenyl ether*, obtained in 90% yield, separates from light petroleum (b. p. 80—100°) in white prisms, m. p. 44—45°, b. p. 185°/9 mm. The *hydrochloride* forms colourless, irregular plates, m. p. 171—173° (Found: HCl, 14·6. $C_{12}H_{10}ONCl,HCl$ requires HCl, 14·3%).

3-*Chloro*-2′-*aminodiphenyl ether* was obtained in 91% yield, and is a colourless oil, b. p. 195°/13 mm. The *hydrochloride*, colourless aggregates of prisms, has m. p. 149—151° (Found: HCl, 14·4%).

The *benzoyl* derivative separates from dilute alcohol in clusters of needles, m. p. 106°.

4-*Chloro*-2'-*aminodiphenyl ether*, obtained in 94% yield by the iron method, and in 84% yield by the alcoholic stannous chloride method, is a yellow oil, b. p. 202°/15 mm. The *hydrochloride* forms colourless prisms, m. p. 190—191° (Found: HCl, 14·3%), and the *benzoyl* derivative, hair-like needles from dilute alcohol, m. p. 108—109°.

Preparation of Phenoxyphenylarsinic Acids.—These acids were prepared by the following modification of the usual method:

The diazo-solution obtained from amine hydrochloride (1 mol.), and hydrochloric acid (1·5 mols.), etc., was neutralised with sodium hydrogen carbonate (0·5 mol.), and treated with a little copper sulphate solution. This solution was then slowly added to an arsenite solution (at 50—60°), containing arsenious oxide (0·75 mol.), sodium hydroxide (2 mols.), sodium carbonate (0·7 mol.), water (7 mols.), and a little copper sulphate. It was found advantageous not to use benzene to prevent frothing, because the by-products were obtained as brown solids which could readily be removed by filtration, the filtrate affording pure arsinic acids after acidification. The acids were dried at 100° before analysis.

o-*Phenoxyphenylarsinic acid* was obtained in 32% yield and separates from alcohol in needles, m. p. 167—168°.

2-o-*Chlorophenoxyphenylarsinic acid*, obtained in 18% yield, crystallises from alcohol or water in needles, m. p. 195—195·5° (Found: As, 22·8. $C_{12}H_{10}O_4ClAs$ requires As, 22·8%).

2-m-*Chlorophenoxyphenylarsinic acid* (yield, 18%) separates from dilute alcohol in rounded, hexagonal plates, m. p. 177—179° (Found: As, 23·0%).

2-p-*Chlorophenoxyphenylarsinic acid* was obtained in 24% yield, and forms cubes (from alcohol), m. p. 187—188° (Found: As, 22·8%).

Preparation of Chlorophenoxyphenyldichloroarsines.—The arsinic acids were reduced in warm concentrated hydrochloric acid suspension with sulphur dioxide in presence of a little potassium iodide. The crude dichloroarsines were converted into the corresponding oxides by dissolving in alcoholic sodium hydroxide containing sodium sulphite, and pouring the product into dilute sulphuric acid. In this way, all traces of iodine were removed, and the oxides, when warmed with concentrated hydrochloric acid, afforded pure dichloroarsines. The yields were almost theoretical.

2-o-*Chlorophenoxyphenyldichloroarsine* is a pale yellow oil, boiling with only partial decomposition at about 217°/8 mm. [Found: Cl (attached to arsenic), 20·7. $C_{12}H_8OCl_3As$ requires Cl, 20·3%].

2-m-*Chlorophenoxyphenyldichloroarsine*, is a pale yellow oil boiling with advanced decomposition at about 220°/10 mm. [Found, Cl (attached to arsenic), 20·8%].

2-p-*Chlorophenoxyphenyldichloroarsine*, pale yellow, prismatic needles from petroleum (b. p. 80—100°), has m. p. 67—68°, and boils with only partial decomposition at about 220°/10 mm. [Found: Cl (attached to arsenic), 20·3%].

The analysis of the dichloroarsines and of the chlorophenoxarsines has been effected by a simplified method: The chloroarsine was dissolved in alcohol, a slight excess of sodium hydrogen carbonate added, the solution warmed, just acidified with dilute sulphuric acid, neutralised with precipitated calcium carbonate, and titrated against $N/10$-silver nitrate.

Preparation of Chlorophenoxarsinic Acids.—8-*Chlorophenoxarsinic acid.* Two grams of 2-*m*-chlorophenoxyphenylarsinic acid were heated with 15 c.c. of concentrated sulphuric acid at 100° for 15 minutes, the solution then poured into water, and the precipitate collected. It was found impossible to obtain a pure compound by recrystallisation, and purification was ultimately effected by adding excess of sodium hydroxide to a solution of the *sodium* salt (colourless leaflets), when the latter was precipitated in the pure state, and gave rise to an acid which crystallised from alcohol in prisms, m. p. 250—252° (Found: As, 24·3. $C_{12}H_8O_3ClAs$ requires As, 24·2%).

7-*Chlorophenoxarsinic acid.* This acid separated on diluting the concentrated sulphuric acid solution; it crystallised from alcohol in colourless plates or prisms, m. p. 240—242° (Found: As, 23·7%).

When *o*-phenoxyphenylarsinic acid or its *o*-chloro-derivative was heated with concentrated sulphuric acid and the product diluted, no separation of solid occurred, and neutralisation by barium carbonate, finally followed by treatment of the barium salt with sulphuric acid, gave deliquescent sulphonic acids, which were not further investigated.

Preparation of Dichlorophenoxarsines.—(a) *From chlorophenoxarsinic acids.* 8-Chlorophenoxarsinic acid, when reduced by the usual method in the warm, gave 5 : 8-*dichlorophenoxarsine*, which separates from petroleum (b. p. 80—100°) in colourless intersecting circular plates, m. p. 125° [Found: Cl (attached to arsenic), 11·5. $C_{12}H_7OCl_2As$ requires Cl, 11·3%].

7-Chlorophenoxarsinic acid, when similarly reduced, gave a mixture which was separated by repeated crystallisation from petroleum–chloroform solution. 5 : 7-*Dichlorophenoxarsine* was obtained as almost colourless rhombs, m. p. 144—145° [Found: Cl (attached to arsenic), 11·3%], together with an arsenic-free *substance* forming yellow laminæ, m. p. 119—120°.

(b) *From chlorophenoxyphenyldichloroarsines.* The dichloroarsines were either allowed to boil gently under reflux under diminished pressure for 6 hours, or heated for a similar period at 200° in a current of carbon dioxide, and the residual crude chlorophenoxarsine was crystallised from chloroform–petroleum mixtures.

5 : 9-*Dichlorophenoxarsine,* from 2-*o*-chlorophenoxyphenyldichloroarsine, forms pale yellow needles, m. p. 99° [Found : Cl (attached to arsenic), 11·3%].

Synthesis of 5 : 8-*Dichlorophenoxarsine.* — 2 : 4-*Dichloronitrobenzene.* As details of the preparation of this substance are not to be found in the literature, they are given here : *m*-Dichlorobenzene (1 mol.) was dissolved in nitric acid (*d* 1·5; 4·5 mols.) with efficient cooling, and the solution then warmed for 10 minutes at 70°. On pouring into ice and water, the nitro-compound separated as a solid, which after being melted under hot water melted at 33° (Beilstein and Kurbatov, *Annalen*, 1876, **182**, 97, give the same figure).

5-*Chloro*-2-*nitrodiphenyl ether.* 2 : 4-Dichloronitrobenzene (1 mol.) was added to a warm solution containing potassium hydroxide (1 mol.), phenol (2 mols.), and water (0·3 mol.). A vigorous reaction at once set in, without addition of copper bronze, and was completed by heating at 100° for 10 minutes. The product, after being worked up as usual, afforded the theoretical yield of the chloronitrodiphenyl ether, which crystallises from alcohol or petroleum (b. p. 80—100°) in prisms, m. p. 85° (Found : Cl, 14·3; NO_2, 17·8. $C_{12}H_8O_3NCl$ requires Cl, 14·2; NO_2, 18·4%). Using half the above proportion of phenol, the same result was obtained.

5-*Chloro*-2-*aminodiphenyl ether.* The last-named nitro-compound was reduced by the iron–ferric chloride method, when the amine hydrochloride was obtained in 95% yield as needles of indefinite m. p. (Found : HCl, 14·2. $C_{12}H_{10}ONCl,HCl$ requires HCl, 14·3%).

4-*Chloro*-2-*phenoxyphenylarsinic acid.* This acid, obtained in 25% yield from the amine hydrochloride in the usual manner, forms colourless, hairy tufts of needles from dilute alcohol, and has m. p. 182° (Found : As, 22·3. $C_{12}H_{10}O_4ClAs$ requires As, 22·8%).

4-*Chloro*-2-*phenoxyphenyldichloroarsine* (see introduction), pale yellow, regular cubes or octahedra from petroleum (b. p. 80—100°), has m. p. 91—92°, and possesses an objectionable odour [Found : Cl (attached to arsenic), 20·1. $C_{12}H_8OCl_3As$ requires Cl, 20·3%].

5 : 8-*Dichlorophenoxarsine.* A weighed quantity of 4-chloro-2-phenoxyphenyldichloroarsine was heated at 200° in a current of pure carbon dioxide. Hydrogen chloride was evolved rapidly, the percentage conversion into dichlorophenoxarsine at the end of 2, 3, and 8 hours being about 45, 55, and 65, respectively. Heating was then discontinued. The product became solid on cooling, and

was once crystallised from light petroleum (b. p. 80—100°). It then melted at 125°, possessed the highly characteristic crystalline form of the dichloroarsine obtained from 2-*m*-chlorophenoxyphenyldichloroarsine, and did not depress the m. p. of this phenoxarsine [Found : Cl (attached to arsenic), 11·7%].

Rates of Conversion of Phenoxyphenyldichloroarsines into Chlorophenoxarsines.—About 1 g. of each of the four dichloroarsines (I—IV) was placed in a test-tube fitted as a wash-bottle, with a capillary carbon dioxide ingress tube passing to the bottom of the test-tube. The egress tube was connected to an absorption flask containing *N*/10-potassium hydroxide solution in each case. All four tubes were simultaneously plunged into a stirred oil-bath kept at 200° ± 1°, and an equal current of pure carbon dioxide allowed to bubble through each. At intervals of 1 hour, the absorption flasks were replaced by similar ones, this operation being carried out in a uniform routine manner, so that the exact time interval obtained for each substance. The results are expressed below in terms of percentage decomposition.

	Percentage decomposition.			
Time (hours).	I.	II.	III.	IV.
1	23·7	1·86	8·90	1·09
2	38·2	6·08	23·4	4·65
3	45·7	11·2	29·3	11·3
4	49·5	15·5	33·0	17·0
5	53·5	19·7	35·5	20·5
6	56·6	24·3	37·8	27·0

The expenses of this investigation were partly defrayed by a grant obtained from the Chemical Society, for which the authors desire to express their thanks.

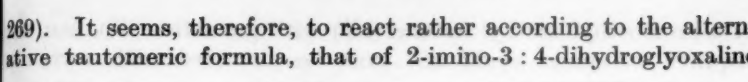
EAST LONDON COLLEGE,
UNIVERSITY OF LONDON. [*Received, June 12th*, 1925.]

CCLXXII.—2-*Amino*-4 : 5-*dimethylglyoxaline*.

By [the late] RICHARD BURTLES and FRANK LEE PYMAN.

4(5)-Amino-5(4)-methylglyoxaline (Fargher, J., 1920, **117**, 668), 4-amino-1 : 5-dimethylglyoxaline, and 5-amino-1 : 4-dimethylglyoxaline (Pyman, J., 1922, **121**, 2616) behave like typical aromatic amines in yielding benzylidene derivatives, and diazo-solutions which couple with sodium β-naphthoxide. The so-called 2-aminoglyoxaline (I), however, neither yields a benzylidene derivative (Fargher and Pyman, J., 1919, **115**, 217) nor does it behave normally with sodium nitrite (Pyman and Timmis, *J. Soc. Dyers Col.*, 1922, **38**,

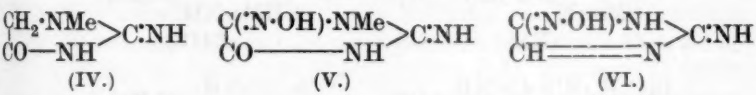
269). It seems, therefore, to react rather according to the alternative tautomeric formula, that of 2-imino-3 : 4-dihydroglyoxaline



(I.) (II.) (III.)

(II), put forward by Fargher and Pyman, and it may be noted that some other amino-compounds capable of similar tautomerism, for example, 2-aminopyridine, fail to react smoothly with nitrous acid.

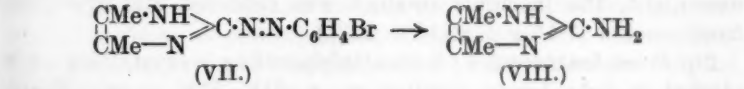
On the other hand, the 8-aminopurines, for example, 8-aminoxanthine (III), which contain an amino-group in the 2-position of the glyoxaline nucleus, yield diazo-compounds which couple with R-salt (H. Fischer, *Z. physiol. Chem.*, 1909, **60**, 69). The 8-aminopurines differ from 2-aminoglyoxaline in that there is no possibility of substitution in their case at the 4- and 5-positions of the glyoxaline ring, and it seemed possible that this difference in structure might be the cause of the difference in behaviour. Some support appeared to be lent to this view by the fact that creatinine (IV) gives with nitric acid and sodium nitrite a mixture of oximinocreatinine (V) with oximinomethylhydantoin (Schmidt and Thumann, *Arch. Pharm.*, 1912, **250**, 352), and it was thought that the action of nitrous acid on 2-aminoglyoxaline might lead to the formation of an oximino-derivative (VI). To test this point, we have prepared



(IV.) (V.) (VI.)

2-*amino*-4 : 5-*dimethylglyoxaline* (VIII), which cannot yield an oximino-compound of this type, and find that in general its behaviour towards nitrous acid in the presence of acid or alkali resembles that of 2-aminoglyoxaline. Consequently, the failure of 2-aminoglyoxaline to behave normally with nitrous acid cannot be attributed to the suggested cause.

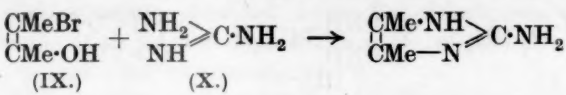
The 2-amino-4 : 5-dimethylglyoxaline (VIII) required for this purpose was prepared by the reduction of 2-p-*bromobenzeneazo*-4 : 5-*dimethylglyoxaline* (VII), which was itself obtained by coupling diazotised *p*-bromoaniline with 4 : 5-dimethylglyoxaline. Since the



(VII.) (VIII.)

synthesis of 4 : 5-dimethylglyoxaline is long and tedious, an alternative method of preparing the amine was sought in the condensation

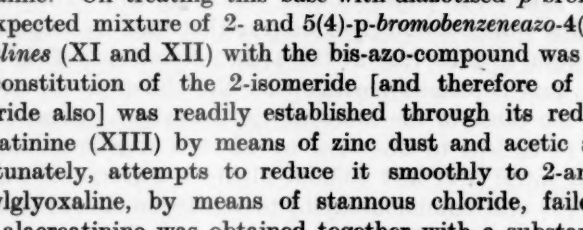
of α-bromoethyl methyl ketone (IX) with guanidine (X), but the required substance could not even be identified with certainty



(IX.) (X.)

amongst the products of the reaction, although an analogous reaction, the condensation of α-chloroketones with thiocarbamides, gives good yields of the 2-amino-4-alkylthiazoles (Traumann, *Annalen*, 1888, **249**, 31).

In these circumstances, attention was directed to the preparation of 2-*amino*-4(5)-*methylglyoxaline* (XIV), which, it was expected, could be made in quantity from the readily accessible 4(5)-methylglyoxaline. On treating this base with diazotised *p*-bromoaniline, the expected mixture of 2- and 5(4)-p-*bromobenzeneazo*-4(5)-*methylglyoxalines* (XI and XII) with the bis-azo-compound was obtained. The constitution of the 2-isomeride [and therefore of the 5(4)-isomeride also] was readily established through its reduction to alacreatinine (XIII) by means of zinc dust and acetic acid, but, unfortunately, attempts to reduce it smoothly to 2-amino-4(5)-methylglyoxaline, by means of stannous chloride, failed. Here again alacreatinine was obtained together with a substance which was probably the required amine.



(XI.) (XIII.)

(XII.) (XIV.)

Experimental.

2-p-*Bromobenzeneazo*-4 : 5-*dimethylglyoxaline* (VII).—4 : 5-Dimethylglyoxaline hydrochloride (4·12 g.) was added to an aqueous solution of hydrated sodium carbonate (59 g.) in water (300 c.c.), and to the turbid liquor, the product of diazotising *p*-bromoaniline (5·37 g.) in concentrated hydrochloric acid (32 c.c.) and water (100 c.c.) with sodium nitrite (3 g.) was added. After keeping over-night, the insoluble product was collected and crystallised from alcohol (7·15 g.; yield = 82%).

2-p-*Bromobenzeneazo*-4 : 5-*dimethylglyoxaline* crystallises from alcohol in light brown needles, m. p. 213—214° (corr.) (Found: N, 19·9; Br, 29·1. $C_{11}H_{11}N_4Br$ requires N, 20·1; Br, 28·7%). It seems to cause irritation of the skin and swelling of the eyelids.

On treatment with cold hydrochloric acid, it yields a sparingly soluble *hydrochloride* (orange-yellow needles, decomp. 135°), which resinifies when heated with dilute hydrochloric acid (Found : Cl, 11·6. $C_{11}H_{11}N_4Br,HCl$ requires Cl, 11·3%).

Reduction.—The above azo-compound (2·79 g.) was reduced by heating at 100° with stannous chloride (5·6 g. hydrated) in concentrated hydrochloric acid (13 c.c.) and water (50 c.c.) until almost completely decolorised. After removing tin by hydrogen sulphide, the solution was concentrated to low bulk, and made alkaline; *p*-bromoaniline was then partly precipitated and partly removed by ether. The mother-liquor was acidified with hydrochloric acid, evaporated to dryness, and extracted with alcohol; the extract gave on evaporation 2-amino-4 : 5-dimethylglyoxaline hydrochloride (1·02 g.; yield = 69%).

2-*Amino*-4 : 5-*dimethylglyoxaline hydrochloride* (VIII) crystallises from alcohol in fine, colourless needles, m. p. 289° (corr.) (Found : C, 40·4; H, 7·0; N, 28·1; Cl, 24·4. $C_5H_9N_3,HCl$ requires C, 40·7; H, 6·8; N, 28·5; Cl, 24·0%). It is very easily soluble in water or alcohol, and is best purified through the carbonate, which is precipitated on mixing this salt with sodium carbonate in strong aqueous solution, and may be recrystallised quickly from water. The *carbonate*, m. p. 144° (corr.), contains 1 H_2O, and is readily soluble in hot water, but much less soluble in cold water. It is insoluble or very sparingly soluble in most organic solvents. Its aqueous solution is alkaline and gradually darkens on heating, yielding resinous products [Found in air-dried substance : C, 43·4, 43·5; H, 7·2, 7·3; N, 28·1. $(C_5H_9N_3)_2,H_2CO_3,H_2O$ requires C, 43·7; H, 7·3; N, 27·8%]. The *picrate* crystallises from water in yellow needles, m. p. 245° (corr.) (Found : N, 24·5. $C_5H_9N_3,C_6H_3O_7N_3$ requires N, 24·7%).

Reactions with Nitrous Acid.—Both 2-amino-4 : 5-dimethylglyoxaline and 2-aminoglyoxaline react sluggishly with nitrous acid in the presence of dilute or concentrated hydrochloric acid or of 25% acetic acid, giving solutions from which neither the original material nor any useful quantity of other crystalline substances could be isolated, but which give deep colours on treatment with sodium hydroxide. A difference in behaviour, however, was observed where 23% nitric acid was employed, for here, after treatment with sodium nitrite and keeping for 2 days, the solution from 2-aminoglyoxaline deposited a red solid, the filtrate from which gave a purple solution with sodium hydroxide, whilst the solution from 2-amino-4 : 5-dimethylglyoxaline remained clear and gave a pale yellow solution with either sodium hydroxide or sodium β-naphthoxide. Both amines give deeply coloured solutions with

either sodium nitroprusside and aqueous sodium hydroxide, or with amyl nitrite and sodium ethoxide in alcoholic solution. Since solutions of both amines in aqueous sodium hydroxide gradually darken on keeping, it is possible that the main effect of nitrous acid upon them is one of oxidation, for both bases are readily oxidised; thus 2-amino-4 : 5-dimethylglyoxaline immediately reduces cold aqueous acid permanganate or ammoniacal silver nitrate.

2-*Acetylamino*-4 : 5-*dimethylglyoxaline*, prepared by boiling the above carbonate with acetic anhydride and fused sodium acetate for 1 hour, crystallised from water in colourless needles, m. p. 270° (corr.) (Found : N, 27·6. $C_7H_{11}ON_3$ requires N, 27·5%). It is soluble in dilute hydrochloric acid and in aqueous sodium hydroxide, but insoluble in aqueous sodium carbonate. After treatment with hydrochloric acid and sodium nitrite, it gives no coloration with sodium β-naphthoxide. It instantly decolorises cold aqueous potassium permanganate.

2-Amino-4 : 5-dimethylglyoxaline does not yield a benzylidene derivative.

p-*Bromobenzeneazo-derivatives of* 4(5)-*Methylglyoxaline*.—The diazo-solution from *p*-bromoaniline (34·4 g.), hydrochloric acid (260 c.c. conc.), water (600 c.c.), and sodium nitrite (14 g.) was added to a stirred ice-cold solution of 4(5)-methylglyoxaline (16·4 g.) and hydrated sodium carbonate (350 g.) in water (1·6 l.). After keeping over-night, the insoluble azo-compounds were collected, and the filtrate was treated with diazotised *p*-bromoaniline (2 g.) [to utilise the 4(5)-methylglyoxaline remaining in excess on account of the formation of the bis-azo-compound], when a further separation of azo-compounds occurred. The total material was extracted several times with cold 2·5% hydrochloric acid (240 c.c. each time), when the very dark-red bis-azo-compound (10 g., crude, m. p. 100—102°) remained undissolved. The filtrate was basified with sodium carbonate, and the product crystallised from alcohol, when nearly pure 2-*p*-bromobenzeneazo-4(5)-methylglyoxaline, *ca.* 20 g., m. p. 219°, separated, followed by crops of lower m. p. (204—210°). The latter were mixed with cold dilute hydrochloric acid, when the sparingly soluble 5(4)-*p*-bromobenzeneazo-4(5)-methylglyoxaline hydrochloride separated, and the filtrate from this, when basified, gave more of the crude 2-azo-compound. After repetition of these operations, there were obtained 25 g. of the 2-azo-compound (47%) and 7·5 g. of the hydrochloride of the 5(4)-azo-compound (12%).

2-p-*Bromobenzeneazo*-4(5)-*methylglyoxaline* (XI) crystallises from alcohol in fine yellow needles, m. p. 225—226° (corr.) (Found: C, 45·2; H, 3·6; N, 21·1. $C_{10}H_9N_4Br$ requires C, 45·3; H, 3·4;

N, 21·1%). Its hydrochloride is very easily soluble in dilute hydrochloric acid.

5(4)-p-*Bromobenzeneazo*-4(5)-*methylglyoxaline* (XII) crystallises from alcohol in irregular, brown prisms, m. p. 238° (corr.) (Found : C, 45·1 ; H, 3·6. $C_{10}H_9N_4Br$ requires C, 45·3 ; H, 3·4%). The *hydrochloride* is sparingly soluble in dilute hydrochloric acid, from which it crystallises in fine yellow needles or long, yellow-red prisms, m. p. 188° (decomp. ; corr.).

Reduction of 2-p-*Bromobenzeneazo*-4(5)-*methylglyoxaline*.—A. *With zinc dust and acetic acid.* Zinc dust (9 g.) was added gradually to a solution of the azo-compound (5·3 g.) in a boiling mixture of glacial acetic acid (20 c.c.) with water (40 c.c.). Zinc was removed by hydrogen sulphide, and the solution was mixed with hydrochloric acid and evaporated to dryness. After basifying with aqueous sodium carbonate, *p*-bromoaniline (2·3 g.) was collected by means of ether, and the aqueous solution was acidified with hydrochloric acid, evaporated to dryness, and extracted with alcohol, which left sodium chloride and some ammonium chloride undissolved. The alcoholic extract was mixed with alcoholic picric acid and gave 1·8 g. (yield 26%) of pure alacreatinine picrate, m. p. 212° (decomp. ; corr. : after sintering earlier) (Found : C, 35·3 ; H, 3·2. Calc. : C, 35·1 ; H, 2·9%). This identification was confirmed by the preparation of the hydrochloride, which had m. p. 202° (corr.) (compare Fargher and Pyman, *loc. cit.*).

B. *With hot stannous chloride.* Stannous chloride (33·6 g., hydrated) in concentrated hydrochloric acid (66 c.c.) was added to a hot solution of the azo-compound (15·9 g.) in hydrochloric acid (12 c.c.) and water (300 c.c.). Decoloration took place at once, and, proceeding as in A, *p*-bromoaniline (6·5 g.), and a mixture of picrates (from water instead of alcohol), amounting to 10·7 g., m. p. 155—180°, were collected. After a tedious process of crystallisation from water and alcohol, the latter gave a sparingly soluble picrate (0·4 g., m. p. >300° ; probably guanidine picrate), alacreatinine picrate (2·3 g. ; m. p. 210—211° ; yield 11%), and 2-*amino*-4(5)-*methylglyoxaline picrate* (XIV) (2·05 g., yield 10%). This salt crystallised from alcohol in brownish-yellow nodules, m. p. 186—187° (corr.) (Found : C, 37·2 ; H, 3·6. $C_4H_7N_3,C_6H_3O_7N_3$ requires C, 36·8 ; H, 3·1%). The hydrochloride, prepared from the picrate in the usual way, was not obtained crystalline, but its aqueous solution resembled that of 2-aminoglyoxaline hydrochloride in its behaviour towards nitrous acid in acid and alkaline solution.

C. *With cold stannous chloride.* Stannous chloride (12·0 g., hydrated) in concentrated hydrochloric acid (30 c.c.) was added to a solution of the azo-compound (6·6 g.) in 3% hydrochloric acid

(66 c.c.) at 0°. After keeping over-night at the laboratory temperature, the solution had become clear and colourless, and was worked up as before, when *p*-bromoaniline (3·5 g.) was obtained together with a mixture of picrates from which 3·2 g. (yield 38%) of pure alacreatinine picrate were isolated.

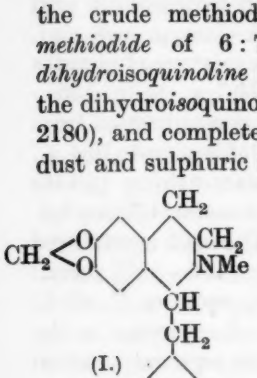
One of us (R. B.) is indebted to the Department of Scientific and Industrial Research for a grant which he desires gratefully to acknowledge.

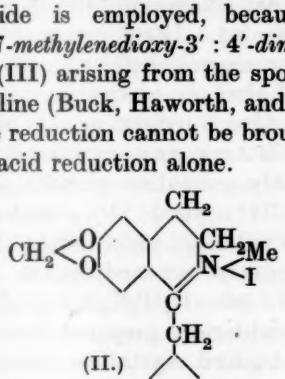
MUNICIPAL COLLEGE OF TECHNOLOGY,
UNIVERSITY OF MANCHESTER. [*Received, July 8th*, 1925.]

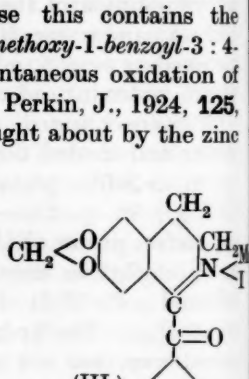
CCLXXIII.—*A Synthesis of* dl-*Dicentrine.*

By ROBERT DOWNS HAWORTH, WILLIAM HENRY PERKIN, jun., and JOHN RANKIN.

THE observation that 1-veratrylnorhydrohydrastinine is converted into 6′-nitroveratrylnorhydrohydrastinine by the action of nitric acid (Haworth and Perkin, this vol., p. 1450) has led to an examination of the action of nitric acid on 1-*veratrylhydrohydrastinine* (I). This base was obtained by converting homoveratroylhomopiperonylamine into 1-veratryl-6 : 7-methylenedioxydihydro*iso*quinoline (Haworth, Perkin, and Rankin, J., 1924, **125**, 1694), the *methiodide* (II) of which was made into the more soluble methochloride, and reduced to 1-veratrylhydrohydrastinine (I), first by zinc dust and sulphuric acid and then electrolytically. This procedure is advisable when the crude methiodide is employed, because this contains the *methiodide* of 6 : 7-*methylenedioxy*-3′ : 4′-*dimethoxy*-1-*benzoyl*-3 : 4-*dihydro*isoquinoline (III) arising from the spontaneous oxidation of the dihydro*iso*quinoline (Buck, Haworth, and Perkin, J., 1924, **125**, 2180), and complete reduction cannot be brought about by the zinc dust and sulphuric acid reduction alone.

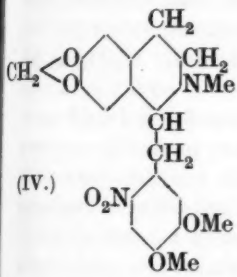
(I.) 

(II.) 

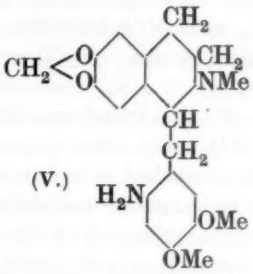
(III.) 

1-Veratrylhydrohydrastinine (I) is a syrup from which a crystalline *hydrochloride*, *hydriodide* and *picrate* have been obtained. When

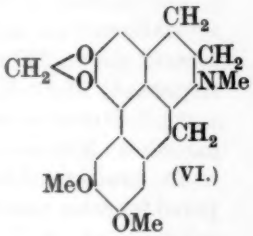
the base (I) was nitrated in acetic acid solution, 6′-*nitroveratryl-hydrohydrastinine* (IV) was obtained as a buff-coloured, crystalline mass, from which a crystalline *hydriodide* and *picrate* have been prepared. The nitro-base (IV) was readily reduced to 6′-*aminover-atrylhydrohydrastinine* (V) by stannous chloride and hydrochloric acid, and although this substance has not been obtained in the crystal-line state, a well-defined *dihydrochloride* has been prepared. The solution of the dihydrochloride yields an intense blue coloration on the addition of ferric chloride, indicating that the positions occupied by the nitro- and amino-groups are those represented in (IV) and (V) respectively.



(IV.)



(V.)



(VI.)

6′-Aminoveratrylhydrohydrastinine (V) was diazotised and treated with copper powder under conditions similar to those which Gadamer employed for the conversion of aminolaudanosine into *dl*-glaucine (*Arch. Pharm.*, 1911, **249**, 680), and a crystalline base, $C_{20}H_{21}O_4N$, m. p. 178—179°, was isolated in a yield of about 15%. The method of synthesis outlined above seems to us to leave no doubt that the synthetical alkaloid is dl-*dicentrine*, and on resolution this should yield an optically active base, identical with naturally occurring dicentrine. We are now engaged in an attempt to prepare considerable quantities of the *dl*-base for the purposes of this resolution and to improve the yields in the various stages of the synthesis; a more complete description of the preparation and properties of these substances is reserved for a future communication. The *dl*-base (VI) yields crystalline salts, the *methiodide* being particularly characteristic, whilst the *hydrochloride* and *picrate* also have been obtained. It should be mentioned that the synthetic base exhibits all those colour reactions with concentrated sulphuric acid, Erdmann's, Fröhde's and Mandelin's reagents which are characteristic of naturally occurring dicentrine (Asahina, *Arch. Pharm.*, 1909, **247**, 202).

Experimental.

1-*Veratryl*-6 : 7-*methylenedioxydihydroisoquinoline Methiodide* (II).—Homoveratroylhomopiperonylamine (20 g.) was converted into 1-veratryl-6 : 7-methylenedioxydihydro*iso*quinoline as described by Haworth, Perkin, and Rankin (*loc. cit.*), the total basic material extracted with benzene, dried over potassium carbonate, concentrated, and boiled with methyl iodide (12 c.c.), when a reddish-brown oil separated which gradually hardened; after 4 hours, the mass of yellow crystals (25 g.) was collected. This crude material, m. p. 228°, was usually employed for reduction purposes.

The *methiodide* is sparingly soluble in water and alcohol, and crystallises from boiling alcohol in beautiful, lustrous, straw-yellow plates, m. p. 239—240° (Found : C, 51·6; H, 4·9. $C_{20}H_{22}O_4NI$ requires C, 51·4; H, 4·7%).

6 : 7-*Methylenedioxy*-3′ : 4′-*dimethoxy*-1-*benzoyl*-3 : 4-*dihydroisoquinoline Methiodide* (III).—As this substance probably occurs in the crude methiodide described above, a small quantity was prepared for comparison with the above methiodide by boiling a benzene solution of 6 : 7-methylenedioxy-3 : 4-dimethoxy-1-benzoyl-3 : 4-dihydro*iso*quinoline (Buck, Haworth, and Perkin, *loc. cit.*) with excess of methyl iodide for several hours, when crystals separated which recrystallised from alcohol in amber-coloured rhombs, m. p. 232—233° (decomp.), sparingly soluble in water and alcohol (Found : C, 50·0; H, 4·2. $C_{20}H_{20}O_5NI$ requires C, 49·9; H, 4·2%).

1-*Veratrylhydrohydrastinine* (I).—The crude methiodide (25 g.) obtained as described above was suspended in water (500 c.c.) and digested with freshly-precipitated silver chloride for 4 hours, filtered off, and reduced with excess of zinc dust and dilute sulphuric acid for ½ hour. After filtration, the pale yellow solution was concentrated to 200 c.c., acidified with dilute sulphuric acid (50 c.c.), and reduced in an electrolytic cell with 5 amperes for 12 hours, when the solution became colourless and a mass of crystals separated. These were dissolved by warming, filtered, the base liberated by the addition of ammonia, extracted with chloroform, dried with potassium carbonate and evaporated, when an oil (12 g.) remained which could not be induced to crystallise. The *hydrochloride* was prepared by dissolving the base in dilute hydrochloric acid, and concentrating, when the salt separated in colourless, rhombic plates, m. p. 215—216°, which are readily soluble in alcohol and water (Found : C, 63·5; H, 6·4. $C_{20}H_{24}O_4NCl$ requires C, 63·6; H, 6·4%). The *hydriodide* was precipitated, by addition of potassium iodide to a hot solution of the hydrochloride, as an oil, which slowly hardened; it crystallised from water containing a little methyl alcohol in colour-

less, elongated prisms, m. p. 180—182° (Found: C, 51·2; H, 5·2. $C_{20}H_{24}O_4NI$ requires C, 51·2; H, 5·1%). It is soluble in methyl or ethyl alcohol, but sparingly so in water. The *picrate* was prepared in alcoholic solution, in which it was sparingly soluble, and crystallised from alcohol–glacial acetic acid in orange-yellow prisms, m. p. 188—189° (decomp.).

6′-*Nitroveratrylhydrohydrastinine* (IV).—Veratrylhydrohydrastinine (5 g.) dissolved in glacial acetic acid (25 c.c.) was treated at 5—10° with concentrated nitric acid (10 c.c.) which had been previously warmed with carbamide. After ¼ hour the dark brown nitration mixture was poured into water, when a brown slime separated. The mixture was digested for ½ hour with excess of ammonia, the liquid decanted from the semi-solid mass, and the latter boiled with dilute hydrochloric acid and animal charcoal, filtered, made alkaline with ammonia, and the crude buff-coloured nitro-base (4 g.) collected. This material is sufficiently pure for reduction purposes, but in order to obtain a pure specimen of the nitro-base, the crude product was dissolved in methyl alcohol, mixed with ether, washed several times with water, the clear ethereal solution dried, concentrated, and diluted with petroleum (b. p. 40—60°) until a turbidity was produced. After some time the nitro-base separated in nodular masses of buff-coloured needles, m. p. 118° (Found: C, 61·8; H, 5·8. $C_{20}H_{22}O_6N_2$ requires C, 62·2; H, 5·7%). It is very soluble in the usual organic solvents with the exception of petroleum, and dissolves in dilute mineral acids to a pale yellow solution. When an acid solution of the base is reduced with zinc dust, the filtered solution gives an intense blue coloration with ferric chloride. The *hydriodide* is precipitated by the addition of potassium iodide to a solution of the base in dilute hydrochloric acid, and crystallises from much alcohol in pale yellow, elongated prisms, m. p. 213°. The *picrate* separates as an oil, which rapidly hardens, when an alcoholic solution of the base is treated with picric acid. It crystallises from glacial acetic acid in lemon-yellow needles, m. p. 192°.

6′-*Aminoveratrylhydrohydrastinine* (V).—6′-Nitroveratrylhydrohydrastinine (10 g.) was dissolved in glacial acetic acid (40 c.c.) and allowed to remain at 15° with hydrated stannous chloride (20 g.) and concentrated hydrochloric acid (40 c.c.) for 12 hours, when a crystalline tin double salt separated. The mixture was poured into water (500 c.c.), filtered, made strongly alkaline with potassium hydroxide, and extracted several times with chloroform; the extracts were dried over potassium carbonate and concentrated. The residual oil was very soluble in organic solvents with the exception of petroleum, and all attempts to induce crystallisation

have failed. The *dihydrochloride* was obtained by dissolving the base in ethyl alcohol and saturating with dry hydrogen chloride, when a mass of small, colourless prisms separated. These are sparingly soluble in methyl or ethyl alcohol, but readily soluble in water, the latter solution giving an intense blue coloration with ferric chloride. It recrystallises from aqueous alcohol in colourless prisms, m. p. 250° (decomp.) (Found : C, 56·1 ; H, 6·2. $C_{20}H_{26}O_4N_2Cl_2$ requires C, 55·9 ; H, 6·1%). The *base* was liberated from the hydrochloride by sodium hydroxide as a colourless, viscid oil.

dl-*Dicentrine* (VI).—The above dihydrochloride (2·5 g.) was dissolved in a little water, made alkaline with sodium hydroxide, and the base extracted with ether, dried, the solvent removed, and the residual oil dissolved in 10% sulphuric acid (10 c.c.). The solution was cooled by the addition of ice (20—30 g.) and 2*N*-sodium nitrite solution (3 c.c.) slowly added. The solution became emerald green and after ½ hour copper powder (1 g.) was added, when nitrogen was rapidly evolved and the solution developed a red coloration. After 3 hours the copper was removed by filtration, the filtrate reduced with zinc dust (1 g.) and concentrated hydrochloric acid (3 c.c.) and again filtered.

A second experiment was carried out on the same scale, and the slightly warm combined filtrates were extracted twice with chloroform. On cooling, *dl*-dicentrine hydrochloride (0·4 g.) separated from the chloroform whilst some non-basic resin remained dissolved. The acid liquors were made alkaline with ammonia and extracted six times with ether, the extracts dried with sodium sulphate, concentrated, and the residual oil was dissolved in boiling 15% hydrochloric acid (10 c.c.), filtered, and cooled, when a further crop of *dl*-dicentrine hydrochloride (0·5 g.) was obtained, the total yield being about 15% of that theoretically possible.

The other products of the reaction have not been closely investigated, but it might be mentioned that some phenolic base and probably also veratrylhydrohydrastinine are present in the dark-coloured hydrochloric acid liquors. Further a dark brown, amorphous substance is precipitated when the acid solution is rendered alkaline with ammonia, which is almost insoluble in ether and has not been further investigated.

dl-*Dicentrine* was obtained by dissolving the hydrochloride in boiling water, neutralising with sodium hydroxide, collecting the cream-coloured base, washing with water, and crystallising from methyl alcohol, when colourless prisms, m. p. 178—179°, were obtained (Found: C, 70·5; H, 6·2. $C_{20}H_{21}O_4N$ requires C, 70·8; H, 6·2%). It is readily soluble in chloroform, ethyl acetate, acetone, benzene, and hot alcohol, moderately soluble in ether and

cold alcohol, and sparingly soluble in petroleum. It dissolves in concentrated sulphuric acid to a colourless solution which rapidly becomes reddish-violet. A colourless solution is obtained with Erdmann's reagent which rapidly becomes greenish-blue, whilst deep blue colorations are developed immediately with Fröhde's and Mandelin's reagents. The *hydrochloride*, obtained by dissolving the base in hot dilute hydrochloric acid, is very sparingly soluble in alcohol and cold water, but crystallises from boiling water in a gelatinous mass or very small, colourless needles which darken at 250° and melt with some decomp. at 263—265° (Found: C, 63·3; H, 5·8. $C_{20}H_{22}O_4NCl$ requires C, 63·6; H, 5·8%). The *methiodide* was obtained by heating the base with a large excess of methyl iodide in a sealed tube at 100° for 1 hour. The methyl iodide was removed by distillation, and the residue extracted with boiling alcohol, from which the methiodide separated on cooling in well-defined, colourless, four-sided plates, m. p. 228—229° (Found: C, 52·7; H, 5·1. $C_{21}H_{24}O_4NI$ requires C, 52·4; H, 5·0%). The *picrate* was prepared in alcoholic solution and crystallised from much alcohol in orange prisms, m. p. 188—189°.

One of us (R. D. H.) is indebted to the Commissioners of the 1851 Exhibition for a studentship which has enabled him to take part in this research, and to the Research Fund Committee of the Chemical Society for a grant which has defrayed some of the expenses of the investigation.

THE DYSON PERRINS LABORATORY,
OXFORD.

[*Received, July 7th*, 1925.]

CCLXXIV.—*Aminobenzthiazoles. Part I. 1-Anilinobenzthiazole and its Tolyl Homologues.*

By ROBERT FERGUS HUNTER.

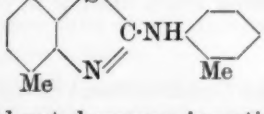
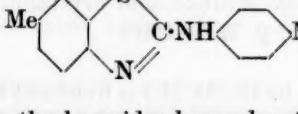
THE objects of this series of investigations are: to synthesise benzthiazoles and allied heterocyclic ring systems from arylthiocarbamides, to study the chemistry of the bromo-addition compounds of the aminobenzthiazoles, and to examine the mobility of the triad system N:C·N[H] ⇌ N[H]·C:N in amino- and substituted aminothiazoles. The synthesis of 1-anilinobenzthiazole (I) from *s*-diphenylthiocarbamide by way of the tetrabromide of the former (Hugershoff, *Ber.*, 1903, **36**, 3121) probably takes place by way of a labile dibromo-addition compound of the thiocarbamide (*loc. cit.*). The thiazole must always be isolated as the tetrabromide and in a sense the ten-

dency to close the thiazole ring is dependent on the tendency to form the bromo-addition compound.

(I.) $C_6H_4<^{S}_{N}>C\cdot NHPh$ $C_6H_4<^{SBr_2}_{NBr_2}>C\cdot NHPh$ (II.)

The physical and chemical properties of 1-anilinobenzthiazole tetrabromide leave little doubt that the compound has a perbromide structure, probably (II): it is reduced by sulphurous acid in the usual way (this vol., p. 1318); on treatment with alkalis, hydroxylic solvents, etc., it passes into dibromoanilinobenzthiazole; and on exposure to air it gradually loses part of its bromine, yielding a stable tribromide.

Hugershoff (*loc. cit.*) observed that di-*o*- and -*p*-tolylthiocarbamides on bromination formed red bromides, which on reduction yielded "tolylaminotoluthiazoles": these must be 1-*o*-toluidino-3-methylbenzthiazole (III) and 1-*p*-toluidino-5-methylbenzthiazole (IV), respectively.

(III.)   (IV.)

He did not, however, investigate the bromides beyond noting that they lost bromine on exposure to air, yielding yellow, crystalline substances.

The first product of bromination of di-*o*-tolylthiocarbamide in chloroform is the red unstable hexabromide (V), whilst di-*p*-tolylthiocarbamide yields a tetrabromide (VI). These lose bromine on exposure to air, yielding stable tribromides; on reduction they are converted into the thiazoles (III and IV, respectively), and on treatment with hydroxylic solvents and alkalis pass into dibromo-1-toluidinomethylbenzthiazoles, $C_6H_2MeBr<^{S}_{N}>C\cdot NH\cdot C_7H_6Br$.

$C_6H_3Me<^{SBr_4}_{NBr_2}>C\cdot NH\cdot C_7H_7$ (V.) $C_6H_3Me<^{SBr_2}_{NBr_2}>C\cdot NH\cdot C_7H_7$ (VI.)

The tribromides resemble the higher bromides in regard to their ease of reduction by sulphurous acid and their conversion into dibromo-substitution products by alkalis, but differ markedly from them in stability. They all crystallise from inert solvents in well-defined crystals of definite melting point and are relatively stable to air. They are, further, incapable of conversion into the higher bromides by bromination.

The conversion of the higher bromides into the tribromides is a mild oxidative change involving the direct elimination of bromine.

In view of the stability of the products it appears reasonable to suggest that they are the hexabromides of condensation products, 1-anilinobenzthiazole tribromide, for example, being

(VII.) $Br_2N<\begin{matrix}C(NHPh)\\C_6H_4\end{matrix}>SBr\cdot SBr<\begin{matrix}C(NHPh)\\C_6H_4\end{matrix}>NBr_2$;

unfortunately, concordant values for the molecular weights have not yet been obtained.

To complete the present study, the bromination of di-*m*-tolylthiocarbamide has been investigated. A red, crystalline hydrobromide was isolated containing seven bromine atoms,

(VIII.) $C_6H_3Me<\begin{matrix}SBr_4\\NBr_2\end{matrix}>C\cdot NH\cdot C_7H_7,HBr$.

The compound yielded a yellow bromide on exposure to air, and on reduction passed into the free base, which may be either 1-*m*-toluidino-4- or -6-methylbenzthiazole. In the absence of definite proof of its structure, it is proposed to term it 1-m-*toluidino*-m-*toluthiazole*.

EXPERIMENTAL.

s-Di-*o*-, -*m*-, and -*p*-tolylthiocarbamides were prepared as described in the literature and melted at 161°, 112°, and 176°, respectively.

1-*Anilinobenzthiazole* (I).—*s*-Diphenylthiocarbamide (50 g.) suspended in 260 c.c. of chloroform was brominated according to Hugershoff's directions (*loc. cit.*). The red needles of the tetrabromide were dried in a vacuum [m. p. 112° (decomp.). Found: Br, 56·8. Calc., Br, 58·6%], suspended in sulphurous acid, and reduced with sulphur dioxide until all solid matter was colourless on crushing. The product was digested with warm 2*N*-sodium hydroxide, the free base washed, dried at 110° (yield quantitative), and crystallised first from ethyl acetate, which is a much better solvent than the alcohol recommended by Hugershoff, and then twice from absolute alcohol; it was thus obtained in small crystals, m. p. 159°. The *acetyl* derivative had m. p. 158° after recrystallisation from ethyl acetate.

The tetrabromide (II) was prepared by heating 1 g. of thiocarbanilide and 1 c.c. of bromine in chloroform under reflux for 2 minutes; on cooling and scratching, fine, red needles separated, which were dried in a vacuum over potassium hydroxide (Found: Br, 58·8%). The substance commences to decompose at about 110°, and melts at 117°. Hugershoff's m. p. of 136° is possibly given erroneously, since even the tribromide melts more than 10° below this temperature.

1-*Anilinobenzthiazole Tribromide* (VII ?).—Bromine was gradually

evolved when 5 g. of the tetrabromide were exposed to the atmosphere for 2 or 3 days. The yellow, crystalline product, m. p. usually about 115°, was recrystallised from chloroform, the *tribromide* being obtained in small, yellow prisms which sintered at about 120° and melted to a clear red liquid at 125° (Found : Br, 51·5. $C_{13}H_{10}N_2Br_3S$ requires Br, 51·7%).

1-o-*Toluidino*-3-*methylbenzthiazole* (III).—Di-*o*-tolylthiocarbamide (10 g.) dissolved in 50 c.c. of chloroform was brominated with 8·5 c.c. of bromine, diluted with an equal volume of chloroform, as in the previous case. The solution, after being heated under reflux for 10 minutes, was either agitated with " dry " ether, when the tribromide of the thiazole separated, or evaporated in a vacuum at room temperature, when a red crystalline crust of a mixture of bromides was obtained; this became yellow at 187°, brown at 205°, red at 230°, viscous and dark at 260°, and melted with charring at 265°. The crude bromide obtained by either method was reduced as in the previous case, and the product was boiled with 2*N*-alkali for a short time. The free base melted below the liquid and hardened on cooling; after being washed and dried, it was crystallised from ethyl acetate, and then from alcohol, being thus obtained in short prisms, m. p. 135° (sintering).

The *acetyl* derivative was obtained in minute crystals sintering at 77°.

1-o-*Toluidino*-3-*methylbenzthiazole Hexabromide* (V).—Di-*o*-tolylthiocarbamide (1 g.) was brominated as in the previous case, and the solution, after being heated under reflux for 3 minutes, was cooled; the fine, red needles of the hexabromide which separated on scratching were dried in a vacuum over potassium hydroxide. They lost bromine at 60° and melted to a clear red liquid at 76—78° (Found : Br, 66·4. $C_{15}H_{14}N_2Br_6S$ requires Br, 65·5%).

The *tribromide* was obtained by exposing 5 g. of the red bromide to the air as in the previous case. After recrystallisation from chloroform it was obtained in small, yellow, glistening prisms, m. p. 250° (decomp.), becoming orange at 205° and red-brown at 240° [Found : Br, 48·7. $(C_{15}H_{14}N_2Br_3S)_2$ requires Br, 48·6%].

Dibromo-1-o-*toluidino*-3-*methylbenzthiazole*.—When boiled with alcohol, either bromide dissolved; thereafter colourless crystals of the *hydrobromide* of the dibromo-substitution product suddenly separated. These, recrystallised from glacial acetic acid and washed with ether, were obtained in lustrous prisms, m. p. 280° (decomp.) (Found : Br, 48·0. $C_{15}H_{12}N_2Br_2S,HBr$ requires Br, 48·7%). The hydrobromide was digested with warm 2*N*-sodium hydroxide, and the free base was recrystallised from glacial acetic acid and washed with ether; tufts of shining needles, m. p. 205°, were obtained, which,

however, retained an appreciable quantity of acetic acid (Found : Br, 32·9%). They were digested with warm alcohol; the base was then obtained in small prisms having the same m. p. as before (Found : Br, 39·3. $C_{15}H_{12}N_2Br_2S$ requires Br, 38·9%).

1-p-*Toluidino*-5-*methylbenzthiazole* (IV).—Di-*p*-tolylthiocarbamide (10 g.) was brominated as in the previous case. The red needles of the tetrabromide were dried in a vacuum and reduced. The free base crystallised from ethyl acetate in hair-like crystals, m. p. 162°.

The *acetyl* derivative was obtained in spherical aggregates of needles, m. p. 158°. The *tetrabromide*, prepared as in the previous case, sintered at 130°, softened at 140°, and melted to a clear red liquid at 145° (Found : Br, 54·9. $C_{15}H_{14}N_2Br_4S$ requires Br, 55·6%). The *tribromide*, obtained by exposing the tetrabromide to the air for some days, crystallised from chloroform in slender, orange needles softening at 145°; m. p. 148° (decomp.) [Found : Br, 49·2. $(C_{15}H_{14}N_2Br_3S)_2$ requires Br, 48·6%].

Dibromo-1-p-*toluidino*-5-*methylbenzthiazole*.—The tribromide was dissolved in boiling alcohol, and the solution concentrated; on scratching and cooling, the *hydrobromide* separated. After recrystallisation from glacial acetic acid it was obtained in small crystals turning yellow at 220°, pale brown at 240°, and melting at 256—258° (Found : Br, 47·8. $C_{15}H_{13}N_2Br_3S$ requires Br, 48·7%). It was treated with warm dilute alkali, and the free base recrystallised from glacial acetic acid and washed with ether, when pale cream crystals were obtained, m. p. 159—160°. They retained an appreciable quantity of solvent as in the case of the *o*-compound (Found : Br, 36·6. $C_{15}H_{12}N_2Br_2S$ requires Br, 38·9%).

1-m-*Toluidino*-m-*toluthiazole*.—Di-*m*-tolylthiocarbamide (4 g.) was dissolved in 40 c.c. of chloroform and brominated with 6 c.c. of bromine diluted with an equal volume of chloroform; heat and hydrogen bromide were evolved and the red bromide was crystalline. The product was dried in a vacuum and reduced by sulphurous acid and sulphur dioxide in the usual way. The base crystallised from ethyl acetate in small, stout, colourless crystals, m. p. 184—186° (Found : S, 11·7. $C_{15}H_{14}N_2S$ requires S, 12·6%).

1-m-*Toluidino*-m-*toluthiazole Hexabromide Hydrobromide*.—Di-*m*-tolylthiocarbamide (1 g.) was dissolved in chloroform and brominated with 1 c.c. of bromine, the solution was refluxed for 3 minutes and allowed to cool slowly in a hot water-bath; the small, four-sided, red tablets which separated were dried in a vacuum over potassium hydroxide. They crumbled to a semi-crystalline, dark mass at 110°, became orange and crystalline at 187°, pale yellow at 197°, and were unmelted above 200° (Found : Br, 69·1. $C_{15}H_{15}N_2Br_7S$ requires Br, 68·9%).

1-m-*Toluidino*-m-*toluthiazole Tribromide Hydrobromide*.—The red bromide was exposed to the atmosphere for some days, and the orange-yellow crystalline residue refluxed with chloroform, in which it was very sparingly soluble. The product consisted of small, yellow crystals of the usual type which softened at 136° and sintered at 190° [Found: Br, 56·3. $(C_{15}H_{15}N_2Br_4S)_2$ requires Br, 55·6%].

The bromide was reduced in the usual way by sulphurous acid and showed the usual stability to air, etc.

In conclusion, the author desires to express his gratitude to Prof. J. F. Thorpe, F.R.S., for the kind interest he has taken in the progress of these experiments.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, April 25th*, 1925.]

CCLXXV.—*The Amino-4-Pyridones.*

By WILLIAM HAUGHTON CROWE.

A COMPARISON of the reactions of the pyridones with those of the aromatic phenols is of considerable interest, and in connexion with the formation of nitro-derivatives and their subsequent reduction it has already been shown that 4 : 6-dimethyl-2-pyridone (Collie and Tickle, J., 1898, **73**, 229) and lutidone (Collie and Hall, J., 1898, **73**, 237) exhibit a formal resemblance to the corresponding xylenols. The simplest pyridones are not very readily accessible and this circumstance no doubt accounts for the fact that their substitution products have not been closely studied. A mononitro-4-pyridone, m. p. 279°, and a dinitro-4-pyridone have now been obtained and reduced; the former by tin and hydrochloric acid to an amino-4-pyridone, and the latter by ammonium sulphide to an aminonitro-4-pyridone. Whilst the work was in progress Koenigs and Freter (*Ber.*, 1924, **57**, 1187) published an account of the nitration of 4-pyridone, but it appears that they did not isolate the nitro-derivatives in a pure condition. Thus they state that the mononitro-derivative has m. p. 269—270° and that the yellow dinitro-compound crystallises with $1H_2O$.

EXPERIMENTAL.

3-*Nitro*-4-*pyridone*.—A mixture of 4-pyridone, fuming nitric acid, and concentrated sulphuric acid was heated on the water-bath for 2 days, poured into water, the acid nearly neutralised with solid sodium carbonate, the solution evaporated to dryness, and the residue extracted with alcohol. The product crystallised from hot

water in yellow needles, m. p. 279° (Found : C, 43·0; H, 3·9; N, 20·2. $C_5H_4O_3N_2$ requires C, 42·9; H, 2·9; N, 20·0%). A concentrated solution gave a lemon-yellow precipitate of the sodium salt on treatment with sodium hydroxide.

3-*Amino*-4-*pyridone*.—Reduction of the nitro-compound with tin and hydrochloric acid proceeded very violently. The solution was diluted with water, the tin removed as sulphide, and the filtrate evaporated on the water-bath; the crystals of the *hydrochloride* thus obtained were dried in a vacuum over sulphuric acid (Found : Cl, 22·0. $C_5H_6ON_2,HCl,H_2O$ requires Cl, 21·6%). The *chloroplatinate* was obtained by treating a concentrated solution of the hydrochloride with platinic chloride and crystallised from hot concentrated hydrochloric acid [Found : C, 18·3; H, 2·5; Pt, 30·1. $(C_5H_6ON_2)_2,H_2PtCl_6,H_2O$ requires C, 18·5; H, 2·5; Pt, 30·1%].

3 : 5-*Dinitro*-4-*pyridone*.—A mixture of 4-pyridone (2 g.), fuming nitric acid (7 c.c.), and concentrated sulphuric acid (13 c.c.) was heated at 140° for about 8 hours and poured into cold water, when 3 : 5-*dinitro*-4-*pyridone* was obtained as a faintly yellow, crystalline precipitate. It crystallised from 50% acetic acid in long, colourless needles (Found : N, 22·9. $C_5H_3O_5N_3$ requires N, 22·7%). A solution in alcohol and acetone gave with sodium ethoxide a brilliant yellow precipitate of the sodium salt.

3-*Nitro*-5-*amino*-4-*pyridone*.—The dinitropyridone was boiled under reflux with the calculated quantity of ammonium sulphide in alcohol, the solid filtered off, and extracted with hot strong hydrochloric acid. On cooling, the *hydrochloride* crystallised in needles, which were recrystallised from concentrated hydrochloric acid with the addition of animal charcoal (Found : C, 31·7; H, 3·5; N, 22·1; Cl, 18·3. $C_5H_5O_3N_3,HCl$ requires C, 31·4; H, 3·7; N, 21·9; Cl, 18·5%). The substance gave yellow solutions, and turned orange in the air, due to loss of hydrogen chloride and formation of the free base.

The author wishes to express his indebtedness to Professor J. N. Collie, F.R.S., for his valuable help and advice during the research, and also to the Department of Scientific and Industrial Research for a grant which made the work possible.

THE RALPH FOSTER LABORATORY OF ORGANIC CHEMISTRY,
UNIVERSITY COLLEGE, LONDON. [*Received, April 13th*, 1925.]

CCLXXVI.—*Researches on Residual Affinity and Co-ordination. Part XXV. A Quadridentate Group Contributing Four Associating Units to Metallic Complexes.*

By GILBERT T. MORGAN and J. D. MAIN SMITH.

FUNDAMENTAL advances were made in the experimental verification of the co-ordination theory when Werner showed that certain compounds and compound radicals were capable of furnishing two associating units to the co-ordination complex surrounding a metallic atom, for by means of such complexes he was able to identify the three-dimensional structure of many co-ordination compounds. Of chemical substances contributing two associating units the following may be cited: ethylenediamine, αα-dipyridyl, dimethyldithiolethylene, and tetramminodihydroxycobaltic bromide, $(NH_3)_4Co(OH)_2Br$, the last of these being noteworthy owing to its completely inorganic character. There are also numerous complex radicals which function as two associating units: the carbonato-, malonato-, and oxalato-groups and the monoenolic radicals of acetylacetone and its homologues, R·CO·CH:C(OH)R′, R and R′ being alkyl or aryl groups. To these compounds and compound radicals capable of occupying two positions in the co-ordination complex the generic name of chelate groups has been given (J., 1920, **117**, 1457) because their tenacious grip of the implicated metallic atom leads to the formation of remarkably stable co-ordination complexes.

Werner also identified groups capable of treble attachment to metallic atoms, such tridentate residues containing three fused chelate groups. The tridentate groups recognised by Werner already contained, however, one metallic atom, so that on association of these tridentate groups with the co-ordinating nuclear atoms the complexes became binuclear, as, for instance, in the case of triamminocobaltic hydroxide, $(NH_3)_3Co(OH)_3$, identified in the complex cation of the salt in which the three hydroxyl groups

$$\left[(NH_3)_3Co\begin{matrix}OH\\OH\\OH\end{matrix}Co(NH_3)_3\right]Br_3$$

contribute simultaneously three units to the co-ordination numbers of each of two cobalt atoms.

Recently Pope and Mann have proved that αβγ-triaminopropane, $NH_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot NH_2$, is capable of treble attachment to metallic atoms. Two molecular proportions of this triacidic base

(*tp*) occupy six co-ordination positions round cobalt and rhodium atoms, forming the complex cations $[Co\ tp_2]'''$ and $[Rh\ tp_2]'''$. This demonstration constitutes the first example of a tridentate non-metallic group in complexes containing a single nuclear atom (*Compt. rend.*, 1924, **178**, 2085; *Proc. Roy. Soc.*, 1925, **107**, 80).

We have now succeeded in identifying a group capable of quadruple attachment to metallic atoms, this being the first known case of a quadridentate group in co-ordination complexes. This quadridentate group is furnished by the bivalent radical of *ethylenediaminobisacetylacetone*, $C_{12}H_{20}O_2N_2$, a compound first prepared by Combes (*Compt. rend.*, 1889, **108**, 1252) on condensing two molecules of acetylacetone with one molecule of ethylenediamine with elimination of two mols. of water. Combes showed that this product is a dienolic diketone,

$CH_3{\cdot}C(OH){:}CH{\cdot}C(CH_3){:}N{\cdot}CH_2{\cdot}CH_2{\cdot}N{:}C(CH_3){\cdot}CH{:}C(OH){\cdot}CH_3$,

yielding a violet cupric salt containing one atomic proportion of copper to one molecular proportion of the dienolic radical.

In attempting to prepare an additive co-ordination compound of cupric acetylacetone and ethylenediamine we obtained accidentally the green monohydrate of Combes's violet salt, copper ethylenediaminobisacetylacetone, which separated from the indigo-blue solution of copper acetylacetone in ethylenediamine hydrate. This observation led to other experiments on Combes's ethylenediaminobisacetylacetone and particularly to the preparation of its *cobaltous* salt,* a non-ionised complex which proved to be dihydrated, and,

$$\left[(H_2O)_2\ Co^{II}\begin{matrix}O\\N\\N\\O\end{matrix}\right\}C_{12}H_{18}\right] \qquad \text{(I.)}$$

as the co-ordination number of bivalent cobalt is usually six, this composition suggested that the organic group might occupy four of the six co-ordination positions. Since, however, the co-ordination number of tervalent cobalt is invariably six, the oxidation of this cobaltous salt in the presence of ammonia should, on the foregoing supposition, lead to a cobaltammine containing two of ammonia and one molecular proportion of the supposed quadridentate group per cobaltic atom with a single univalent acidic ion outside the complex.

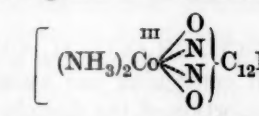
On reaction with ammonium chloride, excess of ammonia, and hydrogen peroxide, this supposition was verified, for the cobaltous salt yielded the anticipated cobaltammine readily and almost

* The co-ordination compounds of ethylenediaminobisacetylacetone with several other bivalent metals have been investigated and will be discussed subsequently.

quantitatively. The chloride radical present was wholly ionised, immediately precipitable with silver nitrate, and yielded the less soluble *bromide*, *iodide*, *chlorate*, *perchlorate*, *nitrite*, *nitrate*, and d-*camphorsulphonate* (Reychler) by double decomposition with the sodium or potassium salts of the corresponding acids.

Excepting the chloride and *d*-camphorsulphonate, all the salts prepared were anhydrous when crystallised from water, thus confirming the view that the cobaltic co-ordination number of six is made up solely of two ammonia molecules and the organic radical. Hence this organic radical, which contributes four to the cobaltic co-ordination number, is actually a quadridentate group.

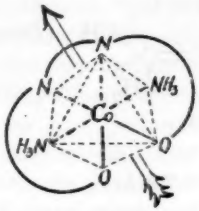
The univalent complex cobaltammine ion is thus demonstrated to have the following chemical constitution:



Five stereochemical arrangements of the groups present in this co-ordination complex are, however, possible, depending on the positions taken up on the octahedron by the ammonia molecules and by the bivalent quadridentate group, $C_{12}H_{18}N_2O_2$ or $-O\cdot C(CH_3){:}CH\cdot C(CH_3){:}N\cdot CH_2\cdot CH_2\cdot N{:}C(CH_3)\cdot CH{:}C(CH_3)\cdot O-$. If the two ammonia molecules are in the antipodal *trans*-positions (Diagram 1) the quadridentate group must be wrapped equatorially round the octahedron. This configuration contains two planes of symmetry and the compound is optically inactive and irresolvable. If the two ammonia molecules are in contiguous *cis*-positions, then three associating units of the quadridentate group must occupy the corners of one triangular face of the octahedron with the fourth associating unit overlapping on to an adjacent face, and this arrangement can be made in four different ways, giving rise to four stereoisomeric modifications. None of these four isomerides possesses a plane, a centre, or an alternating axis of symmetry and hence they are all optically active. Two of them are mirror images of the other two and the four isomerides comprise two enantiomorphous pairs.

Conclusive evidence has now been obtained that the product actually isolated contains two racemoid modifications which have been resolved into optically active forms by *d*-camphorsulphonic (Reychler) acid, and that all these active forms on keeping are spontaneously transformed into the single inactive and irresolvable form. The lack of optical activity in the last indicates that it is the *trans*-form (Diagram 1), in which the pair of ammonia molecules is in the *trans*-octahedral position. The active form with the low optical activity is in all probability the *cis-trans*-form (Diagram 2),

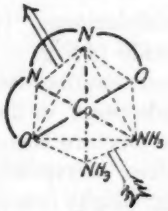
in which only the dyad axis of symmetry of the *trans*-form is retained, the pair of ammonia molecules here being in the *cis*-position while the pair of oxygen atoms is retained in the *trans*-position. The active form with the very high activity may thus be regarded as the *cis*-form (Diagram 3), in which none of the elements of symmetry is retained, the pair of oxygen atoms as well as the pair of ammonia molecules being in *cis*-positions.



Two Planes of Symmetry intersecting in One Dyad Axis of Symmetry.

Diagram 1.

Trans Inactive Isomeride.



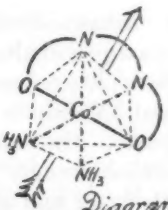
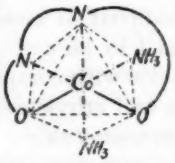
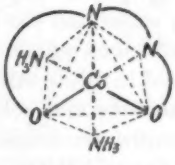


Diagram 2.

Cis-trans Enantiomorphous Pair each with One Dyad Axis of Symmetry and small optical activity.





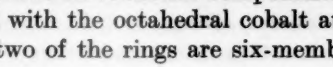
Cis-cis Enantiomorphous Pair without elements of Symmetry and with high optical activity

Diagram 3.

It has not been possible, however, to confirm these structures by chemical means, for the compounds are not decomposed by hot concentrated hydrochloric or hydrobromic acid to yield either the *cis* (violeo)- or *trans* (praseo)-dichlorodiamminoethylenediamminocobaltic halides which could be identified by their respective violet and green colours.

Whatever be the exact chemical structure of the organic group in the complex, the evidence is conclusive that it is a quadridentate

group and moreover that it can be arranged spatially round the co-ordination sphere so as to yield the *cis*- and *trans*-configurations with respect to the ammonia molecules (Diagrams 1, 2 and 3). The tricyclic system of the three chelate components of the quadridentate group associated with the octahedral cobalt atom is shown in plan in Diagram 4; two of the rings are six-membered and one is five-membered.



(*Diagram* 4.)

EXPERIMENTAL.

$C_2H_4(N{:}C{\cdot}CH_3{\cdot}CH{\cdot}CO{\cdot}CH_3)_2$ = ec (ethylenediaminobisacetylacetone).

*Diaquocobaltous Ethylenediamino*bis*acetylacetone*, $[(H_2O)_2\,ec\,Co]$ (Formula I).—Hexa-aquocobaltous chloride (4·8 g. = 1 mol.) was dissolved in hot water (20 c.c.), and ethylenediaminobisacetylacetone (4·5 g. = 1 mol.) and 5*N*-sodium hydroxide (8 c.c. = 2 mols.) added, forming a green paste. On boiling, the mixture turned brownish-yellow and a reddish-orange, crystalline precipitate separated. After washing with water and air-drying, bright orange-red prisms were obtained in yield varying from 85 to 45%, the higher yields being obtained with exclusion of air during the reaction (Found: Co, 18·7. $C_{12}H_{22}O_4N_2Co$ requires Co, 18·6%). The compound was insoluble in water and readily dissolved in most organic solvents to orange solutions which darkened in air owing to oxidation. It readily dissolved in dilute mineral acids with complete decomposition into acetylacetone and cobaltous and ethylenediamine salts.

*Diamminoethylenediamino*bis*acetylacetonocobaltic Chloride Dihydrate*, $[(NH_3)_2Coec]Cl(H_2O)_2$.—This salt was readily obtained in 83% yield on oxidation of the foregoing cobaltous salt by the calculated amount of 6*N*-hydrogen peroxide in the presence of excess of 18*N*-ammonia and ammonium chloride. The salt separated from the cooled mixture in pale fawn needles which were recrystallised from hot water, washed with alcohol, and air dried [Found: Co, 15·2; N (as NH_3), 7·35; H_2O, 8·1. $C_{12}H_{28}O_4N_4ClCo$ requires Co, 15·3; N (as NH_3), 7·25; $2H_2O$, 9·3%).

This feebly coloured cobaltic salt was moderately soluble in water to a brownish-red, neutral solution, from which silver nitrate solution immediately precipitated silver chloride. Concentrated solutions of the appropriate sodium or potassium salts precipitated

the bromide, iodide, nitrite, nitrate, chlorate, perchlorate, and *d*-camphorsulphonate of the complex base from concentrated solutions of the chloride. The chloride dissolved in boiling concentrated hydrochloric or hydrobromic acid solutions, but was not decomposed. It dissolved in boiling caustic soda solution, evolving ammonia and forming a clear reddish-brown solution which appeared to contain the complex diaquo-base. The chloride was quite insoluble in all organic solvents.

The following salts were prepared in quantitative yield by precipitation from concentrated solutions of the chloride by concentrated solutions of the appropriate alkali salt. All except the *d*-camphorsulphonate (Reychler) were very sparingly soluble in water and were precipitated as fine, yellowish-brown needles, which were washed with water and alcohol and air-dried. The camphorsulphonate, which is moderately soluble in water and in moist alcohol, was recrystallised from water and washed with acetone and ether and air-dried.

Bromide, $[(NH_3)_2$ ec Co$]Br$. Found: Co, 14·7; H_2O at 100°, nil. $C_{12}H_{24}O_2N_4BrCo$ requires Co, 14·9%.

Iodide, $[(NH_3)_2$ ec Co$]I$. Found: Co, 13·4; N (as NH_3), 6·4; H_2O at 100°, nil. $C_{12}H_{24}O_2N_4ICo$ requires Co, 13·4; N (as NH_3), 6·3%.

Nitrite, $[(NH_3)_2$ ec Co$]NO_2$. Found: Co, 16·2; N (as NH_3), 7·8; N (as NO_2), 4·0; organic N, 7·6; C, 39·7; H, 6·6; H_2O at 100°, nil. $C_{12}H_{24}O_4N_5Co$ requires Co, 16·3; N (as NH_3), 7·8; N (as NO_2), 3·9; organic N, 7·8; C, 39·9; H, 6·65%.

Nitrate, $[(NH_3)_2$ ec Co$]NO_3$. Found: Co, 15·7; H_2O at 100°, nil. $C_{12}H_{24}O_5N_5Co$ requires Co, 15·7%).

Chlorate, $[(NH_3)_2$ ec Co$]ClO_3$. Found: Co, 14·8; H_2O at 100°, nil. $C_{12}H_{24}O_5N_4ClCo$ requires Co, 14·8%.

Perchlorate, $[(NH_3)_2$ ec Co$]ClO_4$. Found: Co, 14·2; H_2O at 100°, nil. $C_{12}H_{24}O_6N_4ClCo$ requires Co, 14·2%.

d-*Camphorsulphonate*, $[(NH_3)_2$ ec Co$]C_{10}H_{15}O_4S,H_2O$. Found: Co, 10·6; H_2O at 100°, 3·1. $C_{22}H_{41}O_7N_4SCo$ requires Co, 10·6; H_2O, 3·2%.

Resolution of the Racemoid Mixture.—Aqueous solutions of the salts were transparent only in the darker red of the spectrum, and the light of the lithium line 6708 Å. (10^{-8} cm.) was used throughout the polarimetric measurements. Owing to the intensity of colour, solutions stronger than about 1% of the camphorsulphonates and 0·5% of the bromides in 0·5-dcm. tubes could not be used.

cis-dextro-*Bromide.*—On mixing saturated solutions of the complex chloride and the sodium salt of *d*-camphorsulphonic (Reychler) acid, fine, pale fawn needles of the *d*-camphorsulphonate separated,

isolated in six crops, which were washed with acetone and ether and air-dried. The first crop was found to be strongly dextrorotatory. The second crop was redissolved in water and decomposed with a solution of potassium bromide, the complex bromide immediately separating in fine, fawn needles, which were washed with alcohol and ether and air-dried (Found : Co, 14·7%). This bromide was indistinguishable in appearance and general properties from the racemoid bromide, but was strongly dextrorotatory, $[\alpha]_{Li} = +452°$, $[M] = +1784°$. Owing to the evanescent nature of this optical activity it was very fortunate that the specimens were submitted to independent observers.*

cis-trans-dextro-dextro-*Camphorsulphonate.*—The third crop from the above resolution had $[\alpha]_{Li} = +36°$, $[M] = +202·0°$, and deducting $+51·7°$ for the *d*-camphorsulphonate ion, $[M] = +150·3°$ for the cobaltic ion (Found : Co, 19·6%). Subsequent crops possessed successively diminishing activities. Recrystallisation of the crops failed to raise the activity for the cobaltic ion above $[M] = +150°$, and the most soluble crops invariably had a strong lævorotation. The highest lævorotation ever observed was $[M] = -108°$ for the cobaltic ion.

cis-trans-dextro-*Bromide.*—The corresponding *cis-trans-d-d*-camphorsulphonate was decomposed with potassium bromide solution, and the bromide isolated as in the case of the *cis*-bromide (Found : Co, 14·8%). $[\alpha]_{Li} = +40°$, $[M] = +158°$. This *cis-trans*-bromide alone was invariably obtained after the first preparation, and was indistinguishable, except for optical activity, from the racemoid bromide.

Inactive (*or* trans) *Bromide.*—The foregoing optically active salts, on keeping a few days, were found to be completely inactive, the camphorsulphonates having only the activity due to the camphorsulphonate ion, and being irresolvable. Once these inactive salts had been identified, it was found impossible to prepare active salts again. Numerous preparations were performed at ordinary and low temperatures, in sunlight and in darkness, and even in new apparatus in a different building, but optically active salts were never again obtainable. A specimen of the first preparation, which had originally yielded both the *cis*- and the *cis-trans*-bromides, was found to be quite irresolvable after 10 days. We

* A specimen of the racemoid bromide (S. 2) and of the *cis*-bromide (S. 1) was submitted to Mr. C. E. Wood for polarimetric examination without informing him which or if either of the specimens was optically active. His report is as follows : *S.* 1.—Weight, 0·0664 g., dissolved in 12·5 c.c. of water and examined in 0·5-dcm. tube with light of lithium line 6708 Å., $[\alpha]_{Li} = +531°$, $[M] = +2097·4°$. *S.* 2.—Weight, 0·0666 g., dissolved in 12·5 c.c. of water and examined in 0·5 dcm. tube—inactive.—C. E. W.

are unable to assign the precise cause of the inability to obtain active salts after the first ten or so preparations, but it is worthy of remark that active salts could not be obtained after the inactive salts had been brought into existence, pointing to the probability that the result is due to infection. This possibility is not wholly ruled out by preparation in new apparatus in a different building, because the inactive salt may have been a partial product only in later preparations and the active salts simultaneously formed thus infected at the moment of coming into existence. Found for the inactive *bromide*: Co, 14·8%. The inactive bromide was indistinguishable in appearance and general properties from the racemoid and active bromides.

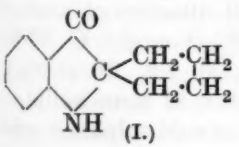
The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research for grants which have helped to defray the expense of this investigation.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON. [*Received, July 15th*, 1925.]

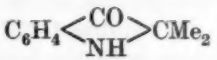
CCLXXVII.—*The Synthesis and Reactions of* 1-*Anilino*-cyclo*pentane*-1-*carboxylic Acid.*

By SYDNEY GLENN PRESTON PLANT and JOHN ERNEST FACER.

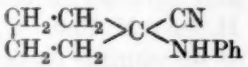
DURING the investigations of the derivatives of tetrahydrocarbazole (Perkin and Plant, J., 1921, **119**, 1825; 1923, **123**, 676) a substance (m. p. 113°) was isolated which appeared to be ψ-indoxyl*spirocyclo*pentane (I). Bucherer and Grolée (*Ber.*, 1906, **39**, 986) have prepared α-anilino*iso*butyric acid (see also Tiemann, *Ber.*, 1882, **15**, 2039; Bischoff and Mintz, *Ber.*, 1892, **25**, 2326) by the hydrolysis of the nitrile obtained from the condensation of aniline with acetone cyanohydrin, and found that it could be made to give very small quantities of 2 : 2-dimethyl-ψ-indoxyl (II) on fusion with a mixture of sodium ethoxide and potassium hydroxide. A similar series of reactions, starting from aniline and *cyclo*pentanone cyanohydrin, ought to yield ψ-indoxyl*spirocyclo*pentane and so establish definitely the constitution of this product, from which several derivatives have been obtained (see also Sidgwick and Plant, this vol., p. 209).



(I.)

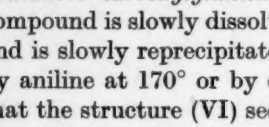


(II.)

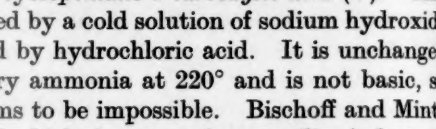


(III.)

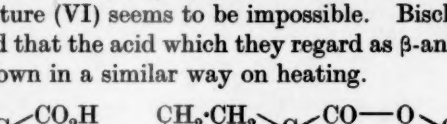
We have now prepared 1-*anilino*-1-*cyano*cyclo*pentane* (III) in this way and converted it into the corresponding *amide*, which can then be hydrolysed to 1-*anilino*cyclo*pentane*-1-*carboxylic acid* (IV). This acid is comparatively unstable and when heated above its melting point loses aniline and water, a substance (m. p. 142°) being formed which appears to be the lactone of 1-1′-*hydroxy*cyclo*pentane*-1′-*carboxylylanilino*cyclo*pentane*-1-*carboxylic acid* (V). This compound is slowly dissolved by a cold solution of sodium hydroxide and is slowly reprecipitated by hydrochloric acid. It is unchanged by aniline at 170° or by dry ammonia at 220° and is not basic, so that the structure (VI) seems to be impossible. Bischoff and Mintz (*loc. cit.*) found that the acid which they regard as β-anilino*iso*butyric acid breaks down in a similar way on heating.



(IV.)



(V.)



(VI.)

Fusion of 1-anilino*cyclo*pentane-1-carboxylic acid with a mixture of sodium ethoxide and potassium hydroxide gave no ψ-indoxyl-*spirocyclo*pentane, but considerable quantities of carbazole were isolated. Many different methods have been investigated for the purpose of eliminating water from the acid at a lower temperature, but without success. The acetyl derivative of 1-anilino*cyclo*pentane-1-carboxylic acid has also been prepared, but this resisted all efforts made to convert it into 6-acetyl-ψ-indoxyl*spirocyclo*pentane.

EXPERIMENTAL.

1-*Anilino*-1-*cyano*cyclo*pentane*.—The bisulphite compound (104 g.) of *cyclo*pentanone was added to water (300 c.c.) and treated with potassium cyanide (38 g.). The *cyclo*pentanone cyanohydrin was extracted with benzene, the solution washed with water and dried over calcium chloride. After the addition of aniline (50 g.), the mixture was boiled for 12 hours and then extracted with half its volume of dilute hydrochloric acid, washed with water, and the solvent removed under diminished pressure. The residue was dissolved in hot petroleum (b. p. 60—80°) and crude 1-*anilino*-1-*cyano*cyclo*pentane* separated, on cooling, as an oil which soon solidified. It was recrystallised from a small quantity of alcohol and obtained in colourless prisms, m. p. 58° (Found: C, 77·5; H, 7·5; N, 15·0. $C_{12}H_{14}N_2$ requires C, 77·5; H, 7·5; N, 15·0%). It decomposes on distillation with the formation of some aniline.

A solution of 1-anilino-1-cyano*cyclo*pentane in cold sulphuric acid

was kept for 2 days and then poured on to ice. On making alkaline with ammonia, the *amide* of 1-*anilino*cyclo*pentane*-1-*carboxylic acid* was precipitated in a pure condition. It separates from alcohol in colourless plates, m. p. 161° (Found : N, 13·5. $C_{12}H_{16}ON_2$ requires N, 13·7%). The *nitrosoamine*, precipitated on addition of sodium nitrite to a solution of the amide in dilute sulphuric acid, separates from alcohol in practically colourless prisms, m. p. 122° (Found : N, 18·0. $C_{12}H_{15}O_2N_3$ requires N, 18·0%).

1-*Anilino*cyclo*pentane*-1-*carboxylic Acid*.—The amide of the acid was dissolved in cold, concentrated hydrochloric acid and almost immediately a precipitate of the hydrochloride separated. The mixture was carefully evaporated to dryness and the residue treated with sodium hydroxide solution till alkaline. After boiling for a short time, the whole was filtered while still hot, and the filtrate acidified with acetic acid, when 1-*anilino*cyclo*pentane*-1-*carboxylic acid* separated as a colourless solid. It crystallised from xylene in colourless prisms, m. p. 162° (Found : N, 6·9. $C_{12}H_{15}O_2N$ requires N, 6·8%).

1-Anilino*cyclo*pentane-1-carboxylic acid is soluble in both acids and alkalis and gives a *nitrosoamine* which can be recrystallised from dilute alcohol and obtained in colourless plates, m. p. 124° (decomp.) (Found : N, 12·2. $C_{12}H_{14}O_3N_2$ requires N, 12·0%).

1-Anilino*cyclo*pentane-1-carboxylic acid, on heating at 230° in a small distillation flask, decomposes and a mixture of aniline and water can be collected. The residue solidifies on cooling, and can be purified by warming first with dilute hydrochloric acid and then with dilute sodium carbonate solution. On recrystallisation from petroleum, the *lactone* of 1-1′-*hydroxy*cyclo*pentane*-1′-*carboxylyl*-*anilino*cyclo*pentane*-1-*carboxylic acid* separates in clusters of colourless prisms, m. p. 142° (Found : C, 72·3; H, 7·3; N, 4·7. $C_{18}H_{21}O_3N$ requires C, 72·2; H, 7·0; N, 4·7%).

An intimate mixture of 1-anilino*cyclo*pentane-1-carboxylic acid (16 g.), sodium ethoxide (48 g.), and potassium hydroxide (40 g.) was gradually heated from 270° to 320° and maintained there for 15 minutes. After cooling, the product was pulverised and added to much water. The undissolved solid was collected, dried, and distilled. The colourless distillate (3 g.), which solidified, crystallised from alcohol in colourless plates, m. p. 238°, of carbazole, identified by analysis (Found : N, 8·5. Calc., N, 8·4%), a mixed melting point determination, and preparation of the picrate, which separated from alcohol in bright red needles, m. p. 184° (compare Schmidt and Schall, *Ber.*, 1907, **40**, 3230).

A solution of 1-anilino*cyclo*pentane-1-carboxylic acid (4 g.) in dry benzene (60 c.c.) was boiled with acetic anhydride (5 c.c.) for

7 hours, the benzene removed under reduced pressure, and the residue treated with acetone–petroleum. 1-*Acetylanilino*cyclo*pentane*-1-*carboxylic acid* crystallises from acetone in colourless prisms, m. p. 195° (Found: N, 5·7. $C_{14}H_{17}O_3N$ requires N, 5·7%).

One of us (S. G. P. P.) wishes gratefully to acknowledge the receipt of a grant from the Chemical Society Research Fund which has defrayed a part of the cost of this investigation.

THE DYSON PERRINS LABORATORY,
OXFORD. [*Received, June 30th*, 1925.]

CCLXXVIII.—*The Action of Nitrogen Dioxide on Anthracene Derivatives.*

By EDWARD DE BARRY BARNETT.

MEISENHEIMER (*Annalen*, 1902, **323**, 205; 1904, **330**, 133) has shown that treatment of anthracene and of 9-nitroanthracene with nitrogen dioxide leads to the addition of nitro-groups to the "bridge" bond with production of dinitro- and trinitro-dihydroanthracene. The action of alkali on these compounds leads to loss of 1 mol. of nitrous acid with re-establishment of the "bridge," but for this purpose pyridine is much more satisfactory and leads to purer products owing to its having no tendency to rearrange the resulting nitro-compound into an oxime (compare Barnett, Cook, and Grainger, J., 1922, **121**, 2065). The facile addition of nitro-groups appears to be common to all anthracene derivatives in which the "bridge" is intact, and in this way the "bridge" exhibits very close analogy to an ethylenic bond (compare Wieland, *Annalen*, 1922, **421**, 2065). The resulting compounds should, in the majority of cases, be capable of existing in *cis*- and *trans*-forms, and as evidence has recently been obtained (Barnett and Matthews, *Rec. trav. chim.*, 1924, **43**, 534; Barnett, Cook, and Matthews, *ibid.*, 1925, **44**, 217, 728, 818) that the geometrical configuration and the stability of compounds formed by addition to the "bridge" are profoundly influenced by the presence of other substituents in the molecule, the action of nitrogen dioxide on several anthracene derivatives has been examined, with the following results.

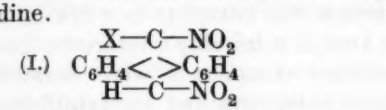
(i) Neither *meso*- nor *Bz*.-substituents have any appreciable influence on the ease with which addition to the "bridge" takes place, 9 : 10-dibromoanthracene, for example, reacting with nitrogen dioxide almost as easily as anthracene itself.

(ii) *Bz*.-Substituents do not increase the stability of the compounds formed by the addition of nitro-groups to the "bridge,"

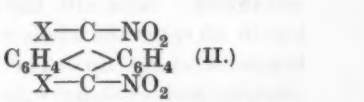
whereas in the case of the addition of halogen atoms, the presence of chlorine atoms in α-positions results in an enormous increase in stability (Barnett and co-workers, *loc. cit.*).

(iii) *Ms.*-Substituents appear to decrease the stability of the 9 : 10-dinitro-9 : 10-dihydroanthracenes.

(iv) Any compound of the general formula I will undergo re-establishment of the " bridge " with great ease on treatment with pyridine.



(I.)



(II.)

If X is a hydrogen atom, this re-establishment is brought about by loss of nitrous acid and formation of a derivative of 9-nitroanthracene. If X is a nitro-group, loss of nitrous acid and formation of a derivative of 9 : 10-dinitroanthracene take place. If X is a halogen atom, loss of halogen acid takes place. This last point is interesting, as Schaarschmidt (*Ber.*, 1924, **57**, 2065; 1925, **58**, 499) has shown that the action of nitrogen dioxide on halogen benzenes, with or without the addition of aluminium chloride, leads to the production of nitrohalogen benzenes, the *p*-isomeride predominating, often almost to the complete exclusion of the *o*-isomeride. In Schaarschmidt's experiments intermediate additive compounds were undoubtedly formed (and actually isolated in the impure state in combination with aluminium chloride). Since these lose nitrous acid rather than halogen acid, their structure must be different from that of those additive compounds formed by addition to an anthracene " bridge." This difference may be due to addition having taken place to a double bond (Kekulé formula). Alternatively, addition may have taken place to a " bridge " (Dewar formula), the different behaviour of the benzene and anthracene derivatives lying in their geometrical configuration, *cis-* in the case of anthracene derivatives, *trans-* in the case of benzene derivatives. Owing to the very unstable nature of the additive compounds it is extremely difficult to decide which of these alternatives is correct.

(v) Compounds of the general formula II, where X represents halogen, are extremely unstable and pass readily at the ordinary temperature into 9-nitro-9-halogen anthrone (when X is bromine) or into the corresponding anthraquinone (when X is chlorine).

(vi) When the molecule is unsymmetrical, loss of nitrous acid from a derivative formed by the addition of nitrogen dioxide may or may not lead to the same nitro-compound as is formed by loss of water from the compound (nitrodihydroanthranol) obtained by the addition of nitric acid to the " bridge."

EXPERIMENTAL.

Nitrogen dioxide generated by heating a mixture of lead nitrate and sand was passed into a solution or suspension of the anthracene derivative in chloroform, the whole being well cooled in a freezing mixture. The increase in weight gave the amount of nitrogen dioxide used; except where otherwise stated, it was found best to use excess. As a rule the reaction was complete in a few minutes, but in all cases the whole was kept in a freezing mixture for an hour before working up. The additive compounds were isolated by diluting and washing with light petroleum and recrystallising the solid, usually from luke-warm chloroform–light petroleum. Owing to the unstable nature of the additive compounds, recrystallisation is often very troublesome, and it was generally found best not to attempt to crystallise more than a gram at a time. The products can only be dried in a vacuum desiccator at the ordinary temperature, and they retain solvent very obstinately. They are all colourless, crystalline solids.

9-Nitroanthracene and 9 : 10-dinitroanthracene (m. p. 310°, not 294° as given in the literature) were prepared very easily by the action of cold pyridine and alcohol on the additive compounds obtained from anthracene and 9-nitroanthracene respectively.

1-Chloroanthracene gave an additive compound, which, owing to its slight power of crystallisation, could not be obtained pure. The crude substance on treatment with pyridine and alcohol in the cold gave 1-*chloro*-9 (*or* 10)-*nitroanthracene* (golden-yellow needles from alcohol or glacial acetic acid, m. p. 155°) which is different from the chloronitro-compound produced by the action of pyridine on the additive compound obtained from 1-chloroanthracene and nitric acid (Barnett and Matthews, *Rec. trav. chim.*, 1924, **43**, 538) (Found: N, 5·4. $C_{14}H_8O_2NCl$ requires N, 5·4%).

2-Chloroanthracene gave an additive compound which could only be obtained as a viscous oil. This with pyridine and alcohol gave a yellow solid which was obviously a mixture of isomeric chloronitro-compounds, but no simple method of separation was found.

1 : 5-*Dichloro*-9 : 10-*dinitro*-9 : 10-*dihydroanthracene* was obtained from 1 : 5-dichloroanthracene. It retains chloroform very obstinately; the sample analysed had been recrystallised, although with very heavy loss, from warm acetone (Found: N, 8·0. $C_{14}H_8O_4N_2Cl_2$ requires N, 8·3%). On heating, it turns yellow and then melts at 156° with violent evolution of gas. With cold pyridine and alcohol it passes very readily into 1 : 5-dichloro-9-nitroanthracene.

The additive compound from 1 : 8-dichloroanthracene could not

be obtained free from solvent, and a sample dried for 5 days in a vacuum desiccator gave a strong carbylamine reaction (Found: N, 5·7 after 1 day, 5·65 after 5 days. $C_{14}H_8O_4N_2Cl_2,1\frac{1}{2}CHCl_3$ requires N, 5·4%). It melts at 215° with violent evolution of gas, after turning yellow at a much lower temperature. On treatment with cold pyridine and alcohol it gave the same 1 : 8-dichloro-9 (or 10)-nitroanthracene as is obtained by the action of pyridine on the additive compound of nitric acid and 1 : 8-dichloroanthracene (Barnett and Matthews, *loc. cit.*).

9-*Bromo*-9 : 10-*dinitro*-9 : 10-*dihydroanthracene*.—The quantities used were 4 g. of nitrogen dioxide, 10 g. of 9-bromoanthracene, and 20 c.c. of chloroform. The solid collected after keeping for an hour and identified after recrystallisation as 9 : 10-dibromoanthracene was a by-product and was not present in the original 9-bromoanthracene. The main product, twice recrystallised, was colourless; on heating, it turned yellow and then sintered at about 115°, but had no definite melting point (Found: N, 8·0. $C_{14}H_9O_4N_2Br$ requires N, 8·0%). 9 : 10-Dinitroanthracene was the sole product obtained by the action of pyridine and alcohol.

9-*Bromo*-9-*nitroanthrone*.—The quantities were 5 g. of nitrogen dioxide, 10 g. of 9 : 10-dibromoanthracene, and 25 c.c. of chloroform; the period of keeping was about 2 hours. The product, recrystallised twice, formed colourless, silky needles which sintered at 116° and agreed in their general properties with the description of 9-bromo-9-nitroanthrone given by Meisenheimer (*Annalen*, 1904, **330**, 181) (Found: N, 4·45. Calc., N, 4·4%). This compound passes into anthraquinone very easily. The reaction is probably decomposition rather than hydrolysis, as it was completed in a few minutes when the compound was added to boiling benzene which had been dried for several weeks over metallic sodium.

9 : 10-*Dichloro*-9 : 10-*dinitro*-9 : 10-*dihydroanthracene*.—The solid obtained from 7 g. of nitrogen dioxide and 12·5 g. of 9 : 10-dichloroanthracene in 50 c.c. of chloroform was washed with cold chloroform–light petroleum and then twice recrystallised from chloroform. It is extremely unstable and decomposes almost at once into anthraquinone on boiling with chloroform, but by working with amounts of about 0·5 g., dissolving these in chloroform at 30°, and at once cooling the solution in a freezing mixture, snow-white crystals were obtained. Owing to the rapid decomposition which takes place at the ordinary temperature it was found necessary to analyse the product after drying it for an hour in a vacuum desiccator over concentrated sulphuric acid (Found: N, 8·0. $C_{14}H_8O_4N_2Cl_2$ requires N, 8·3%).

1 : 5 : 9-*Trichloro*-9 : 10-*dinitro*-9 : 10-*dihydroanthracene*.—The product from 3 g. of nitrogen dioxide and 7 g. of 1 : 5 : 9-trichloroanthracene in 15 c.c. of chloroform, after being twice crystallised, was a slightly yellow, crystalline powder which on heating decomposed with violent evolution of gas at 156° (Found in material dried for 3 hours: N, 7·4. $C_{14}H_9O_4N_2Cl_3$ requires N, 7·5%).

1 : 5-*Dichloro*-9 : 10-*dinitroanthracene* was obtained by the action of cold pyridine and alcohol on the above trichlorodinitrodihydroanthracene. After being twice recrystallised from pyridine, it formed pale yellow needles, m. p. 277° (Found: N, 8·3. $C_{14}H_6O_4N_2Cl_2$ requires N, 8·3%).

2 : 3 : 9-*Tribromo*-9-*nitroanthrone*.—Excess of nitrogen dioxide was passed into a well-cooled suspension of 10 g. of 2 : 3 : 9 : 10-tetrabromoanthracene in 50 c.c. of chloroform, and the whole kept for 3 hours in a freezing mixture. Unchanged tetrabromoanthracene was removed, the filtrate diluted with light petroleum, and the solid which separated washed with light petroleum and then twice recrystallised from warm chloroform–light petroleum (Found: N, 2·8. $C_{14}H_6O_3NBr_3$ requires N, 2·9%). When heated with toluene, this product evolves brown fumes and passes quantitatively into 2 : 3-dibromoanthraquinone.

The products obtained by the action of nitrogen dioxide on anthranyl methyl ether, 9-phenylanthracene or 9-phenylanthranyl methyl ether were, not additive compounds, but 9-nitroanthrone, 9-nitro-10-phenylanthracene and 9-phenyl-9-hydroxyanthrone respectively, all of which were identified by direct comparison with authentic samples.

SIR JOHN CASS TECHNICAL INSTITUTE,
LONDON, E.C. 3.

[*Received, July 6th*, 1925.]

CCLXXIX.—*The Constitution of Indian Kamala. Part I.*

By SIKHIBHUSHAN DUTT.

KAMALA was first investigated by Anderson, who isolated from it a crystalline compound, rottlerin, $C_{11}H_{10}O_3$ (*Edin. New Phil. J.*, 1855, **1**, 300). This has been investigated by various chemists, including A. and W. Perkin (*Ber.*, 1886, **19**, 3109), A. G. Perkin (J., 1893, **63**, 975), Jawein (*Ber.*, 1887, **20**, 182), Telle (*Arch. Pharm.*, 1906, **244**, 441), Bartolotti (*Gazzetta*, 1894, **24**, ii, 480). A. G. Perkin (J., 1895, **67**, 230) obtained from it *o*- and *p*-nitrocinnamic acids, *p*-nitrobenzaldehyde, and *p*-nitrobenzoic acid by the action

of fuming nitric acid, and acetic and benzoic acids and phloroglucinol by fusion with potassium hydroxide. The present investigation was undertaken with a view to elucidate further the constitution of the substance.

Benzene is the most suitable solvent for extracting the colouring matter from kamala, as it dissolves very little of the resin. The pure colouring matter is best crystallised from toluene. The m. p. (206—207°) of the rottlerin isolated by the author is 15° higher than that recorded by A. G. Perkin (Telle, *loc. cit.*, gives m. p. 203—204°); the two substances, however, appear to be almost identical in chemical properties.

On treatment with acetic anhydride rottlerin yields a colourless, crystalline *hepta-acetyl* derivative melting at 165°; Perkin isolated a hexa-acetyl derivative as a yellow, crystalline powder melting at 130—135°. Possibly rottlerin contains, in addition to six phenolic hydroxyl groups, an alcoholic hydroxyl group which can be acetylated only under suitable conditions. In support of this view is the fact that only *hexamethoxy* and *hexabenzoyl* derivatives are obtainable from rottlerin by the action of methyl sulphate and benzoyl chloride in presence of dilute sodium hydroxide solution —conditions under which an alcoholic hydroxyl group is scarcely attacked at all.

Acetylrottlerin and acetylmethoxyrottlerin form dibromo-additive compounds. This indication of the presence of a double bond in rottlerin is supported by the fact that the action of fuming nitric acid on the substance produces a large quantity of *p*-nitrocinnamic acid.

On fusion with potassium hydroxide rottlerin yields phloroglucinol as the only phenolic compound, and on oxidation with permanganate acetyl- and methoxy-rottlerin are converted into triacetyl- and trimethyl-phloroglucinoldicarboxylic acids, respectively. These facts indicate that rottlerin contains two phloroglucinol residues joined to the parent structure by either one or two side chains; if by one side chain, an alkyl substituent is present in the phloroglucinol nucleus. Moreover, as phthalic and terephthalic acids are almost always formed in the oxidation of rottlerin, there appear to be two more benzene nuclei in its molecule, containing side chains in ortho-positions in the one and in para-positions in the other. The two acids, however, may be produced by selective elimination of a side chain from the same benzene nucleus containing three side chains in the 1 : 2 : 4-positions. This alternative is the more probable, for the presence of five benzene nuclei would account for thirty out of the thirty-three carbon atoms in the molecule of rottlerin; there would remain

only three carbon atoms, two of which must be present in the side chain containing the double bond. In all probability, therefore, rottlerin contains four benzene nuclei, of which (1) two must be phloroglucinol residues, (2) one must be in the residue $C_6H_5 \cdot CH:CH \cdot C$, and (3) one must be a benzene nucleus containing at least three side chains.

Rottlerin is converted into a ketone, rottlerone, by the action of 2% sodium carbonate solution (Perkin, *loc. cit.*), and therefore appears to contain a secondary alcoholic hydroxyl group.

As Telle (*loc. cit.*) seems to have isolated the mono-, di-, and trimethyl ethers of phloroglucinol from the products of interaction of barium hydroxide solution, and of sodium hydroxide and zinc dust, and rottlerin, the phenolic hydroxyl groups in this would appear to be more or less methylated. The present author, however, obtained a negative result in the estimation of methoxyl by Zeisel's method. The phenolic portion of the rottlerin molecule is completely destroyed by the action of oxidising agents, but phenolic derivatives are obtained in large yields by oxidation of acetyl- and methoxy-rottlerin, in which the phenolic hydroxyl groups are protected from the action of the oxidising agent.

From the ease with which cinnamic acid and dihydrocinnamic acid are produced from rottlerin by the action of oxidising and reducing agents respectively, it seems that the molecule contains a group $C_6H_5 \cdot CH:CH \cdot CO \cdot$ or $C_6H_5 \cdot CH:CH \cdot C(OH)<$. The presence of this would account for the formation of benzaldehyde, benzoic acid, and their derivatives by the action of various reagents..

Experimental.

Preparation of Rottlerin.—Commercial kamala (150 g.) was passed through a 100-mesh sieve and heated under reflux with 1200 c.c. of benzene for 8 hours. The solution was filtered at once and again after 12 hours and concentrated to about 200 c.c. The colouring matter, which separated slowly in large, brownish-yellow plates, was washed with alcohol and twice recrystallised ftom toluene; rottlerin was thus obtained in large, glistening, brownish-yellow plates, m. p. 206—207° (yield about 9 g.) (Found: C, 69·2; H, 5·5; *M*, ebullioscopic in toluene, 585, 615, 598, by silver salt, 675. Calc. for $C_{33}H_{30}O_9$, C, 69·4; H, 5·2%; *M*, 570).

The substance is sparingly soluble in the usual organic solvents. In doiling toluene and amyl alcohol it dissolves to the extent of about 12%, but separates almost completely on cooling. It is very soluble in basic solvents like pyridine, quinoline, or aniline and also in alkali hydroxides and carbonates.

Acetylrottlerin, $C_{33}H_{23}O_9(C_2H_3O)_7$, prepared by boiling pure

rottlerin with acetic anhydride (5 parts) and a few drops of pyridine and crystallised from dilute acetone, acetic acid, and alcohol, was obtained in colourless needles, m. p. 165° [Found: C, 64·9; H, 5·2. $C_{33}H_{23}O_9(C_2H_3O)_7$ requires C, 65·3; H, 5·0%]. An estimation of acetyl by Perkin's method confirmed the presence of 7 such groups.

Dibromoacetylrottlerin, $C_{33}H_{23}O_9Br_2(C_2H_3O)_7$.—Acetylrottlerin and bromine (in slight excess of 1 mol.) were allowed to react in cold glacial acetic acid. The mixture, which was not completely decolorised on gentle warming, was poured into water; the precipitate crystallised from carbon disulphide in pale yellow, microscopic needles, m. p. 145° [Found: Br, 15·2. $C_{33}H_{23}O_9Br_2(C_2H_3O)_7$ requires Br, 15·6%].

Benzoylrottlerin, $C_{33}H_{24}O_9(C_6H_5{\cdot}CO)_6$, obtained by the Schotten-Baumann method, was a light yellow powder which could not be crystallised from any solvent. It was moderately soluble in most of the organic solvents, insoluble in alkali hydroxides, and did not melt below 300° (Found: C, 75·8; H, 4·5. $C_{75}H_{54}O_{15}$ requires C, 75·3; H, 4·5%).

Methoxyrottlerin, $C_{33}H_{24}O_3(OMe)_6$.—Rottlerin dissolved in 5% aqueous sodium hydroxide was shaken with excess of methyl sulphate, more alkali and methyl sulphate were added, and the process was repeated four or five times, the solution being kept alkaline. The mixture was then warmed on the water-bath for 1 hour and the yellow solid was collected after cooling and dissolved in ether. The ethereal solution was exhaustively extracted with dilute sodium hydroxide solution, and the ether evaporated; the residue crystallised from dilute acetic acid in pale yellow, microscopic needles, m. p. 135—137° [Found: C, 71·1; H, 6·9; OMe, 28·8. $C_{33}H_{24}O_3(OMe)_6$ requires C, 71·5; H, 6·4; OMe, 28·4%].

Acetylmethoxyrottlerin, $C_{33}H_{23}O_3(OMe)_6{\cdot}C_2H_3O$.—A mixture of 2 g. of methoxyrottlerin, 10 c.c. of acetic anhydride, and 1 drop of pyridine was boiled for ½ hour and poured into water. The colourless product crystallised from acetic acid in fine clusters of needles, m. p. 215—217° [Found: C, 70·2; H, 6·6. $C_{33}H_{23}O_3(OMe)_6{\cdot}C_2H_3O$ requires C, 70·7; H, 6·3%].

Dibromoacetylmethoxyrottlerin, $C_{33}H_{23}O_3Br_2(OMe)_6{\cdot}C_2H_3O$.—The procedure was that for preparing dibromoacetylrottlerin. The pale yellow product, which could not be crystallised, decomposed on heating and was moderately soluble in most of the organic solvents [Found: Br, 18·2. $C_{33}H_{23}O_3Br_2(OMe)_6{\cdot}C_2H_3O$ requires Br, 18·6%].

Action of Oxidising Agents on Rottlerin and its Derivatives.—(1) *Fuming nitric acid.* Rottlerin (10 g.) was gradually added to 50 c.c. of nitric acid (*d* 1·5), the temperature being always kept

below 0°. The colouring matter dissolved very easily and torrents of red fumes were evolved. After 1 hour, the mixture, which had become almost solid owing to separation of *p*-nitrocinnamic acid, was diluted somewhat with ice-cold nitric acid (*d* 1·4) and filtered; the crystals melted at 285° after crystallisation from alcohol. A further quantity of *p*-nitrocinnamic acid was obtained on pouring the nitric acid mother-liquor into ice-water. The filtrate on extraction with ether yielded a gum from which succinic acid was isolated. Acetic acid was detected in the mother-liquor. No *o*-nitrocinnamic acid, *p*-nitrobenzoic acid, or *p*-nitrobenzaldehyde could be isolated (compare Perkin, *loc. cit.*). *p*-Nitrobenzaldehyde and *p*-nitrobenzoic acid were formed in fairly good quantity if the mixture was allowed to warm during the reaction, but even so, no *o*-substituted derivative could be isolated.

(2) *Dilute nitric acid* (*d* 1·2). Rottlerin (10 g.) was heated on the water-bath for 72 hours with 200 c.c. of dilute nitric acid with occasional shaking; the brownish-yellow colour of the rottlerin had then disappeared and the liquid was thick with white crystals. The mixture was filtered; acetic acid was detected in the filtrate. The crystals gave benzoic acid on distillation in steam; the non-volatile portion, on repeated extraction with boiling water, yielded almost colourless needles of *p*-nitrobenzoic acid, m. p. 237°. A small quantity of phthalic acid was obtained by evaporating the aqueous filtrate to dryness and crystallising the residue from boiling water.

The residue left after extraction with boiling water was insoluble in almost all solvents. Heated under diminished pressure, it sublimed in long needles of terephthalic acid (the methyl ester melted at 139°, alone or mixed with methyl terephthalate) (Found: C, 57·5; H, 3·9; Ag in silver salt, 57·2. Calc., C, 57·8; H, 3·6; Ag, 56·8%).

(3) *Alkaline potassium permanganate.* Rottlerin (5 g.) dissolved in 250 c.c. of 3% sodium hydroxide solution was treated with 1% potassium permanganate until this was no longer decolorised. The solution was filtered, concentrated to small volume, and acidified. The white precipitate was distilled in steam, small quantities of benzoic and acetic acids passing over. The non-volatile residue, on extraction with hot water, yielded a small quantity of phthalic acid, while the aqueous mother-liquor, on extraction with ether, yielded an unidentified dibasic acid, $C_{18}H_{20}O_4$, which crystallised from glacial acetic acid in glistening prisms, m. p. 192°. The aqueous mother-liquor after extraction with ether contained oxalic acid (isolated as calcium salt). The insoluble residue left after all these operations was terephthalic acid.

(4) *Alkaline hydrogen peroxide.* The same substances are obtained by the prolonged action of hydrogen peroxide on a cold alkaline solution of rottlerin as by the action of potassium permanganate; some benzaldehyde also is produced and the yield of the unknown acid is greater.

(5) *Alkaline potassium ferricyanide.* The reaction, which was very slow in the cold, was completed in several hours in the warm. On acidifying the alkaline solution, a tarry mass was obtained, which on distillation in steam yielded small quantities of benzaldehyde and benzoic acid. From the dark brown, brittle residue, which was very soluble in alkali or ether, nothing definite could be isolated. On oxidation with alkaline permanganate, it yielded a mixture of phthalic and terephthalic acids and also a small quantity of another acid, m. p. 216°. The last appears to be a tribasic acid from the analysis of its silver salt, but it was not obtained in sufficient quantity for further examination.

(6) *Potassium persulphate.* Rottlerin (5 g.) dissolved in 150 c.c. of concentrated ice-cold sulphuric acid was gradually treated with 14 g. of finely powdered potassium persulphate with stirring, until carbon dioxide was no longed evolved. The solution, which became colourless after being stirred for 2 hours, was poured on to ice, and the precipitate collected; acetic acid was detected in the filtrate. The precipitate was separated by steam distillation into volatile benzaldehyde and benzoic acid and non-volatile phthalic and terephthalic acids with only traces of cinnamic acid. The unknown dibasic acid, which is an almost constant oxidation product of rottlerin, was not formed.

(7) *Fusion with potassium hydroxide.* Ten grams of rottlerin were gradually added to 100 g. of potassium hydroxide and 10 c.c. of water at 100°; the mixture was then heated at 180—200° for ½ hour. The cold melt was dissolved in water, acidified with concentrated hydrochloric acid, extracted with ether, and the ether evaporated. The dark brown, viscous mass thus obtained, which had a strong odour of acetic acid, gave, on steam distillation, acetic and benzoic acids. An ethereal extract of the residue, on decoloration with animal charcoal and concentration at the ordinary temperature, yielded large, transparent leaflets of phloroglucinol, m. p. 218°. The ethereal mother-liquor on complete evaporation left a brown gum from which nothing definite could be isolated.

Action of Reducing Agents.—(1) *Zinc dust and sodium hydroxide.* A mixture of 5 g. of rottlerin, dissolved in 150 c.c. of 5% sodium hydroxide, and 20 g. of zinc dust was heated on the water-bath for 1 hour, and the colourless solution was filtered and acidified with hydrochloric acid. The yellowish-white, viscous mass obtained,

on distillation in steam, gave an acid distillate from which small quantities of succinic and acetic acids were isolated. The non-volatile residue, on cooling, solidified to a brown, brittle mass, from which dihydrocinnamic acid was isolated by extracting the powdered substance with sodium bicarbonate solution. The final dark brown residue could not be crystallised, nor could anything definite be isolated from it. It gave a dark violet coloration with ferric chloride, dissolved in sodium hydroxide or carbonate solution with a dark brown colour, and on fusion with potassium hydroxide at 200°, yielded comparatively large quantities of phloroglucinol.

(2) *Tin and hydrochloric acid.* A mixture of 10 g. of rottlerin with 20 g. of tin dust was heated with 150 c.c. of fuming hydrochloric acid on the water-bath with frequent stirring until all the tin had dissolved. The mass was diluted with water and filtered hot. The filtrate on extraction with ether yielded small quantities of acetic and succinic acids. The tarry residue on extraction with sodium bicarbonate yielded 1·3 g. of dihydrocinnamic acid. The residue, which could not be crystallised, yielded phloroglucinol on fusion with potassium hydroxide.

(3) *Sodium hyposulphite.* Rottlerin in alkaline solution, on treatment with sodium hyposulphite, yielded a brown, tarry mass, from which only dihydrocinnamic acid could be isolated.

(4) *Hydriodic acid and red phosphorus.* A mixture of 5 g. of rottlerin, 2 g. of red phosphorus, and 20 c.c. of hydriodic acid (*d* 1·75), when heated in a sealed tube at 230—250° for 6 hours, developed great pressure, due to what was probably a gaseous aliphatic hydrocarbon, and separated into two layers. The upper, dark brown, oily layer, isolated by means of ether, distilled between 135° and 260°; decomposition then set in. The largest fraction, b. p. 145—160°, on redistillation gave, between 152° and 159°, a colourless liquid with an odour resembling that of mesitylene. It was probably *n*-propylbenzene (Found: C, 89·7; H, 10·2. Calc., C, 90·0; H, 10·0%), but only a small quantity was available for examination. When heated with fuming nitric acid, it yielded a very small quantity of a crystalline acid, m. p. 140°, which did not depress the m. p. of *m*-nitrobenzoic acid.

(5) *Pyrogenic reduction with zinc dust.* Ten grams of rottlerin were distilled with zinc dust in the usual way in a stream of hydrogen. Gaseous hydrocarbons were evolved. The distillate which was collected in a receiver cooled in a freezing mixture consisted of a mixture of a crystalline solid and a liquid. The latter was absorbed in porous plate; the solid, crystallised from alcohol, gave colourless plates, m. p. 190°, of β-methylanthracene and yielded β-methylanthraquinone on oxidation with nitric acid.

The liquid, extracted from the porous plate with ether, was colourless, had b. p. 230—240°, and could not be identified; it was not obtained in sufficient quantity for analysis or quantitative examination.

Oxidation of Acetylrottlerin with Permanganate.—Acetylrottlerin (20 g.) suspended in 500 c.c. of water was oxidised at 80° with 25 g. of potassium permanganate in 5% solution, kept neutral by the addition of 10 g. of copper sulphate. The excess of permanganate was destroyed by ferrous sulphate, and the solution filtered. The filtrate, on evaporation to a small volume and acidification, yielded a small quantity of benzoic acid; the mother-liquor contained oxalic and acetic acids.

The precipitated oxides of manganese, iron and copper were suspended in water and dissolved by passing a current of sulphur dioxide. The brown, crystalline residue was extracted with boiling water, and from the solution a small quantity of phthalic acid was obtained. The insoluble residue, on extraction with alcohol, left terephthalic acid. The alcoholic extract, after decoloration with animal charcoal and dilution with hot water, yielded triacetylphloroglucinoldicarboxylic acid in glistening prisms, m. p. 260—270° (decomp. and evolution of carbon dioxide) (Found: C, 49·2; H, 3·7; Ag in the silver salt, 39·4. Calc. for $C_{14}H_{12}O_{10}$, C, 49·4; H, 3·5%. Calc. for $C_{14}H_{10}O_{10}Ag_2$, Ag, 38·9%). The ethyl ester, prepared in the usual way, melted at 96° and was identical with that described by Moore (J., 1904, **85**, 167). On deacetylation with concentrated sulphuric acid in absolute alcohol, the acid yielded ethyl phloroglucinoldicarboxylate, m. p. 106° (Moore, *loc. cit.*).

On heating in a vacuum at 220°, the acid evolved carbon dioxide. The melt was dissolved in ether, washed with very dilute sodium hydroxide, decolorised with animal charcoal, and the solution evaporated; colourless prisms, m. p. 105°, of triacetylphloroglucinol were thus obtained. When this was hydrolysed by solution in strong sulphuric acid, phloroglucinol was produced in quantitative yield.

Oxidation of Methoxyrottlerin with Permanganate.—Methoxyrottlerin was oxidised by a boiling neutral solution of potassium permanganate and the reaction products were isolated in the ways described above. Benzoic, acetic, phthalic, and terephthalic acids were obtained together with trimethylphloroglucinoldicarboxylic acid, which crystallised from dilute alcohol in glistening, white needles, m. p. 248—255° (decomp. and evolution of carbon dioxide) (Found: C, 51·3; H, 4·8; Ag in the silver salt, 46·4. Calc. for $C_{11}H_{12}O_7$, C, 51·5; H, 4·6%. Calc. for $C_{11}H_{10}O_7Ag_2$, Ag, 45·95%). The acid was heated at 240° for ½ hour until the evolution of carbon

dioxide had ceased, and then distilled. A colourless liquid passed over at 250—255° and solidified in the receiver to a crystalline mass of glistening leaflets, m. p. 50—51°, of trimethylphloroglucinol. This gave a quantitative yield of phloroglucinol on hydrolysis with concentrated hydriodic acid.

The greater part of this work was done in the Laboratories of the Dacca College and the Dacca University during 1921–1923. My best thanks are due to Mr. Nirmal Kumar Sen for his help in the preparation of large quantities of rottlerin, and to Dr. E. R. Watson and Dr. P. C. Ghosh for their kind encouragement during the progress of the work.

IMPERIAL COLLEGE, LONDON, S.W.7. [*Received, June 30th,* 1925.]

CCLXXX.—*The Decomposition of Carbon Monoxide in the Corona due to Alternating Electric Fields. Part I.*

By MIGUEL CRESPI and ROBERT WINSTANLEY LUNT.

IN the course of experiments repeating the work of Moser and Isgarischeff (*Z. Elektrochem.*, 1910, **16**, 613) on the decomposition of carbon dioxide when submitted to the corona produced by alternating electric fields of commercial frequencies, one of the authors (R. W. L.) observed the formation of a solid substance the properties of which appeared to be similar to those of the solid obtained by Brodie when investigating the action of the electric discharge on carbon monoxide (*Annalen*, 1873, **169**, 270; *Proc. Roy. Soc.*, 1873, **21**, 245). The chief characteristics assigned to the solid by Brodie were a dark brown colour, high solubility in water and alcohol (the former solution giving a marked acid reaction), and a very low solubility in ether. Basing his arguments on the composition of the gas phase before and after exposure to the discharge, Brodie stated that there appeared to be two oxides, possibly two of a series, to which he assigned the formulæ C_4O_3 and C_5O_4. Four years later, Berthelot (*Ann. Chem. Phys.*, 1877, **10**, 72) repeated some of Brodie's work and assigned the formula C_4O_3 to the solid substance he prepared.

In view of the scanty information existing on this interesting compound of carbon and oxygen experiments have been carried out with the aim of describing in some detail the properties of this material and the conditions under which it is produced. The difficulties encountered in producing appreciable quantities of the

solid substance have occasioned some delay in completing a survey of its properties and this communication will therefore be confined to an account of the behaviour of carbon monoxide when subjected to alternating electric fields of frequency 250 over the pressure range 760 to 80 mm. Hg.

Experimental.

Description of Apparatus.—Source and Measurement of Electric Power. Single-phase alternating current of frequency 250 was supplied from a motor alternator set and transformed up to the required voltage over the range 2000 to 10,000 volts. The voltage applied to the reaction vessel was measured by a Kelvin-White instrument and the current flowing through it was indicated approximately by a dynamometer type milliameter reading 0—50 milliamperes.

Reaction Vessel. A glass vessel fashioned in the usual manner of a Siemen's ozoniser, that is to say, constructed of concentric cylinders, served to contain the gas during exposure to the discharge. One end of the inner tube was closed and the other was ground to fit into the outer tube; it could therefore be removed from the outer tube when necessary. Surrounding the outer tube was a glass jacketing tube which was filled with mercury and served as the high-tension electrode. The inner tube was filled with mercury and constituted the other electrode, which was earthed. It was cooled by a stream of water at room temperature flowing through a thin-walled glass tube immersed in the mercury. The temperatures of each electrode were recorded by alcohol thermometers, it having been observed that mercury thermometers rapidly fouled under the experimental conditions obtaining.

The reaction vessel was so arranged that carbon monoxide could be fed in from a reservoir or the vessel connected to a Töpler pump; it was also connected to a mercury manometer. The volume of gas in the connecting capillary tubes which was out of contact with the discharge was reduced to a minimum. The diameters of the outer wall of the vessel were 22·4 mm. (external) and 21 mm. (internal), and of the inner wall 16 mm. (external) and 14·8 mm. (internal). The length of electrodes was approx. 300 mm.

Preparation of Carbon Monoxide.—The gas produced by dropping recrystallised formic acid into an evacuated flask containing warm sulphuric acid was passed over solid potash and dried by flowing through some 6 feet of tubing packed with phosphorus pentoxide. It was analysed by exposure to alkaline pyrogallol and by absorption in ammoniacal cuprous chloride solution, in which the gas was completely soluble. The gas so prepared was free from oxygen.

Measurements and Results.—Two sets of observations were carried out, one at 4500 volts and the other at 9000 volts. In every case the heat generated in the reaction vessel was sufficient to raise the mean temperature of the vessel several degrees above the room temperature despite the cooling of the inner electrode.

In order to follow the pressure change during exposure to the discharge it became necessary to know the value of the mean temperature of the vessel, T_m, corresponding to any two given values of the temperature of the outer and inner electrodes, T and T_1, respectively. The following empirical relationship was observed to hold

$$\log T_m = k \log T_1 + (1 - k) \log T$$

with an accuracy of about 1%. The value of k was determined in several cases by observing the pressure of the gas, p_1, corresponding to electrode temperatures, T and T_1, and the pressure, p_2, of the same gas when the whole system was allowed to reach a uniform temperature, T_2. We then have

$$(T_m + 273)/(T_2 + 273) = p_1/p_2.$$

Substituting the values so obtained for T_m in the above equation, the mean value of k was found to be 0·737.

Preliminary experiments established that the sole products of the reaction were the brown solid, which is deposited on the walls of the reaction vessel, and a residual gas mixture of carbon monoxide and dioxide, containing not more than traces of oxygen.

The experimental procedure was to introduce carbon monoxide into the evacuated reaction vessel and to record the pressure of the gas in the reaction vessel and the temperature of the two electrodes every quarter of an hour from the commencement of the discharge until sensible equilibrium was reached, as indicated by the cessation of pressure change.

After discontinuing the discharge, the residual gas was pumped off and analysed by absorbing the carbon dioxide present with solid potash. Knowing the composition of this residual gas and the values of the gas pressure before and after exposure to the discharge, the composition of the solid substance produced can readily be calculated.

The brown solid deposited on the walls of the vessel has no appreciable vapour pressure.

The results are given in Tables I and II: p_0 and p_∞ are the initial and the equilibrium pressure (mm. of Hg at 0°) of the gas in the reaction vessel; t is the time (mins.) required to reach sensible equilibrium; a is the ratio C/O in the solid; and b is the ratio CO/CO_2 in the equilibrium gas mixture.

TABLE I.

Voltage applied to reaction vessel = 4500 volts r.m.s.
Current flowing through reaction vessel = 1·0 milliamperes (approx.).

p_0.	p_∞.	a.	b.	t.	$(p_0 - p_\infty)/t$.
501·7	344·0	1·204	11·89	225	0·70
317·6	219·1	1·228	11·00	150	0·66
201·4	145·4	1·256	11·76	75	0·74
141·6	110·1	1·335	12·93	60	0·86
105·3	83·2	1·348	13·59	35	0·63
78·7	61·5	1·409	11·22	25	0·69
			mean 12·07		mean 0·71

TABLE II.

Voltage applied to reaction vessel = 9000 volts r.m.s.
Current flowing through reaction vessel = 2·5 milliamperes (approx.).

p_0.	p_∞.	a.	b.	t.	$(p_0 - p_\infty)/t$.
501·0	327·5	1·186	11·27	225	0·77
304·7	213·4	1·267	10·11	135	0·68
193·3	140·8	1·274	11·04	90	0·61
130·8	100·2	1·308	12·63	35	0·87
94·4	73·7	1·398	11·49	25	0·82
			mean 11·82		mean 0·77

The curves representing the velocity of reaction can be derived from the following expression :—

$$-dp_t/dt = (k + tk')(p_t - p_\infty),$$

where p_t denotes the pressure at any time t, and k and k' are constants which appear to be functions of the initial pressure and of the electrical conditions, although the time required to reach sensible equilibrium seems to be practically independent of the latter. The form of these functions remains to be determined. The observed values of p_t and those calculated from the above equation are set forth in Tables III and IV; the agreement obtaining is satisfactory and not uninteresting. The values of the mean rate of decrease of pressure, which are cited in the sixth column of Tables I and II show a remarkable constancy.

The wide range of electrical and pressure conditions obtaining being borne in mind, one of the most interesting results is the constancy observed in the composition of the residual gas when equilibrium is reached. This approximates closely to a mixture of one volume of carbon dioxide with twelve volumes of carbon monoxide.

The composition of the solid substance appears to be independent of the electrical conditions over the range examined, and solely dependent on the gas pressure, the ratio of carbon to oxygen in the solid substance increasing continuously with decreasing gas pressure.

TABLE III.

Voltage applied to reaction vessel = 4,500 volts r.m.s.
Pressures as before in mm. Hg. (0°).

	k = 0·0127. k' = 0·00023.		k = 0·0102. k' = 0·00062.		k = 0·0828. k' = 0·00388.		k = 0·0801. k' = 0·00679.	
Time in mins.	p obs.	p calc.	p obs.	p calc.	p obs.	p calc.	p obs.	p calc.
0	501·7	501·7	317·6	317·6	141·6	141·6	105·3	105·3
5	—	—	—	—	—	—	98·0	98·0
10	—	—	—	—	—	—	91·5	91·5
15	474·9	474·4	296·6	294·0	119·2	119·2	87·2	87·1
30	447·5	446·4	272·0	274·0	111·2	111·2	—	—
35	—	—	—	—	—	—	83·2	83·2
45	419·1	420·5	251·5	252·3	—	—		
60	398·0	398·2	238·4	236·6	110·1	110·1		
75	381·0	380·5	229·0	227·1	—	—		
90	367·5	367·4	223·2	222·2	—	—		
105	358·5	358·5	—	—	—	—		
120	—	—	—	—	112·4	110·1		
150	—	—	219·1	219·1	—	—		
195	344·2	344·2	—	—	—	—		
225	344·0	344·0	—	—	—	—		

TABLE IV.

Voltage applied to reaction vessel = 9,000 volts r.m.s.
Pressures as before in mm. Hg. (0°).

	k =0·00581. k'=0·00018.		k = 0·043. k'= 0.		k =0·0547. k'=0.		k =0·0700. k'=0.		k =0·232. k'=0.	
Time in mins.	p obs.	p calc.	p obs.	p calc.	p obs.	p calc.	p obs.	p calc.	p obs.	p calc.
0	763·3	763·3	501·0	501·0	304·7	304·7	130·8	130·8	94·4	94·4
5	—	—	—	—	—	—	109·4	110·9	80·7	80·2
10	—	—	—	—	—	—	103·2	103·9	75·8	75·7
15	—	—	434·8	432·9	247·4	253·6	101·6	101·5	74·4	74·3
20	—	—	—	—	—	—	—	100·7	73·9	73·9
25	—	—	—	—	—	—	100·8	100·4	73·7	73·7
30	728·8	727·8	385·5	391·6	227·9	231·1	—	100·3	—	—
35	—	—	—	—	—	—	100·2	100·2	—	—
45	—	—	361·4	366·5	224·5	211·1	—	—		
60	675·4	674·5	350·8	351·2	220·8	216·8	—	—		
75	—	—	—	—	218·5	214·9	—	—		
90	621·9	622·2	—	—	—	—	102·8	100·2		
120	582·7	583·1	333·6	330·7	213·9	213·5	—	—		
135	—	—	—	—	213·4	213·4	—	—		
225	—	—	327·5	327·6	—	—	—	—		
300	541·5	541·5	—	—	—	—	—	—		

This observation is in agreement with the work of the General Electric Company's Research Staff on the disappearance of carbon monoxide in discharge tubes when operated at pressures less than 1 mm. of mercury (*Phil. Mag.*, 1920, **40**, 585). They were of the opinion that at such pressures the monoxide decomposed to carbon and the dioxide, although no chemical tests were made to establish the formation of carbon.

In addition to possessing the properties recorded by Brodie and Berthelot the solid substance is very hygroscopic. In view of the small quantities of material available up to the present time the systematic examination of its chemical properties is reserved for a later communication.

Summary.

(1) A description has been given of the behaviour of carbon monoxide in the corona due to alternating electric fields of frequency 250. It decomposes giving a solid substance, containing carbon and oxygen, and a mixture of carbon dioxide and monoxide of approximately constant composition.

(2) The composition of the solid substance appears to be independent of the electrical conditions and varies solely with the gas pressure.

(3) In so far as the properties of the solid substance have been examined they are similar to those recorded by earlier investigators. In addition the substance has been found to be highly hygroscopic.

(4) Experiments are in progress to determine more completely the nature of the solid substance.

The authors wish to tender their thanks to the Ramsay Memorial Fellowship Trust for a Fellowship (M. C.) and to the Commissioners for the Exhibition of 1851 for a Senior Studentship (R. W. L.) which have enabled them to carry out this research, and particularly to Professor F. G. Donnan, F.R.S., for his deep interest and advice during the progress of the research.

The William Ramsay Inorganic and Physical Chemistry Laboratories,
University College, London. [*Received, May 27th,* 1925.]

CCLXXXI.—*Anode Phenomena in the Electrolysis of Potassium Ethyl Malonate.*

By John Braithwaite Robertson.

R. E. Gibson (this vol., p. 475) has shown that the synthesis of trichloromethyl trichloroacetate by electrolysis of trichloroacetic acid takes place only when the anode potential exceeds 2·34—2·37 volts on the hydrogen standard and concluded that the anode process is one of direct oxidation. However, as he points out, this is not a carbon to carbon synthesis, and it appeared desirable to determine whether similar results would be obtained in a true Kolbe synthesis.

As in the apparatus devised for measuring anode potentials, only small currents could be employed, and therefore only small quantities of synthetic product obtained, potassium ethyl malonate proved to be a very suitable material because, whereas this salt is very soluble in water, the diethyl succinate formed on synthesis is an oil and sparingly soluble in the solution employed. On production of this oil a change in the appearance of the gas bubbles leaving the anode was easily observable, as Gibson found to be the case with trichloroacetate. When no synthesis occurred, these were small in size and left the anode freely, but as soon as the oil was formed they became much larger and appeared to cling to the anode, a phenomenon attributable to their being coated with a thin film of the synthetic oil.

Preliminary experiments showed that a change occurred at a potential of about $\epsilon_H = 2{\cdot}3$, where ϵ_H is potential referred to the normal hydrogen electrode as standard. Below this potential the gas evolved at the anode was chiefly oxygen, whereas above this potential scarcely any oxygen was produced, the gas being almost pure carbon dioxide.

A series of determinations was carried out to fix this point more exactly. Measurements were made at different values of the applied *E.M.F.* between the electrodes of (1) the anode potential, (2) the current, and (3) the volume and composition of the gases evolved in unit time. Similar measurements were also made when electrodes of (1) platinised platinum, (2) grey platinum, and (3) gold were used. The apparatus employed is practically identical with that described by Gibson, except that here it was not necessary to have the anode and the cathode in separate compartments.

The potential difference between the anode and a calomel electrode was measured by the compensation method, with use of an Ostwald decade rheostat, a battery of accumulators, a sensitive galvanometer, and a standard cadmium cell. The current passing through the electrolyte was measured on a milliamperemeter, and the *E.M.F.* between the electrodes on a shunted voltmeter.

After all necessary connexions had been made, the current was switched on and the voltage adjusted to give the desired *E.M.F.* between the electrodes. Readings of the anode potential were made at intervals. The potential took a considerable time to become constant, in general about an hour, but in some cases several hours; with gold electrodes within a certain range no steady reading was obtained even after a constant *E.M.F.* had been applied for 12 hours. When equilibrium was reached, the evolved gases were collected for a measured length of time varying from $\frac{1}{2}$ hour to 3 hours (depending on the current passing) until

at least 20 c.c. were obtained. During this time frequent regular readings of anode potential and current were made, and the means of these were taken as representing the potential and current during the period. If these readings varied by more than a few hundredths of a volt or a few milliamperes, as the case might be, the experiment was abandoned. The amount of hydrogen found on analysis served as a check on the amperemeter readings. It was necessary to determine only the carbon dioxide and oxygen in the gas sample, the residue being hydrogen. Several tests with fuming sulphuric acid showed that no unsaturated hydrocarbon gases were produced.

The results are detailed on p. 2060 : c is the current in milliamperes, ϵ_H the anode potential, and CO_2 and O_2 are the volumes (c.c at *N.T.P.*) evolved per hour.

The solution used in each case was *N*-potassium ethyl malonate. The values for carbon dioxide do not represent the total carbon dioxide produced, as a considerable proportion of this remains in the solution, being fixed as carbonate or bicarbonate by the alkali formed round the cathode, but they are useful for purposes of comparison.

The diagrams show curves for oxygen evolved per hour and current carried plotted from the above data, the numbers of the diagrams corresponding with those of the tables on p. 2060.

With smooth platinum electrodes (IB) there is, between anode potentials of 2·30 and 2·37, a sudden drop in oxygen evolved. A similar drop, although not so sharp, occurs with grey platinum electrodes (IG) at a potential of about 2·4. The characteristic change in the nature of the bubbles leaving the anodes was also apparent about these points. This value of 2·3—2·4 therefore corresponds to the potential at which the synthesis of diethyl succinate occurs. A large-scale experiment with grey platinum electrodes and a current of 1 ampere showed that above this potential synthesis took place as with smooth platinum, a film of oil appearing on the surface of the electrolyte after about 15 minutes. This value of the anode potential is the same as that found by Gibson (*loc. cit.*) in the formation of trichloromethyl trichloroacetate. The shape of the current curve, however, differs from his. Whereas he found a drop in the curves on formation of the ester, here a fairly sharp rise takes place. In order to determine whether the difference was due to the different natures of the reactions or simply to differences in apparatus and working conditions, Gibson's experiment was repeated using the apparatus already described but replacing the platinum foil anode by one of platinum wire. With *N*-trichloroacetic acid, a similar curve to Gibson's was obtained.

Ib.

Electrodes : Two pieces of bright platinum foil, each 20 × 25 mm., 1 cm. apart.

$c.$	ϵ_H.	CO_2.	O_2.
20	2·02	0·7	2·3
24	2·12	0·7	3·0
31	2·16	1·5	4·1
37	2·27	1·7	5·3
44	2·30	2·1	6·2
63	2·37	4·0	2·6
88	2·39	7·0	2·5
123	2·45	20·6	0·5

Ig.

Electrodes : Grey platinum. Two pieces of foil, 10 × 10 mm., which had been platinised, then gently ignited in a spirit lamp flame, 1·5 cm. apart.

$c.$	ϵ_H.	CO_2.	O_2.
36	2·28	0·4	6·1
42	2·31	0·6	6·6
54	2·35	1·5	7·8
73	2·40	2·3	8·2
84	2·44	3·5	7·3
105	2·49	4·4	7·6
181	2·6—2·7	9·2	5·8

II.

Electrodes : Platinised platinum wire, 2 cm. long and 0·5 mm. in diameter, 1·5 cm. apart.

$c.$	ϵ_H.	CO_2.	O_2.
24	2·24	0·1	5·0
31	2·29	0·1	6·0
38	2·32	0·1	7·5
53	2·43	0·1	10·1
65	2·53	0·3	12·9
91	2·68	0·4	17·1
103	2·77	0·7	19·3
121	2·88	1·1	22·3
135	3·00	1·5	24·7
142	3·10	1·9	25·6
168	3·25	3·7	29·2
185	3·33	7·0	29·1
202	3·50	19·7	21·9
210	3·78	18·4	14·5

III.

Electrodes : Gold wires, 1 mm. in diameter, 1 cm. apart. In the first six experiments these were 2·5 cm. long. The length was then reduced to 0·5 cm. With a similar anode potential the current carried was then exactly 1/6th of that given with the larger electrodes. The actual results obtained for current and gases evolved in the first six experiments have been divided by 6 to make the whole series comparable.*

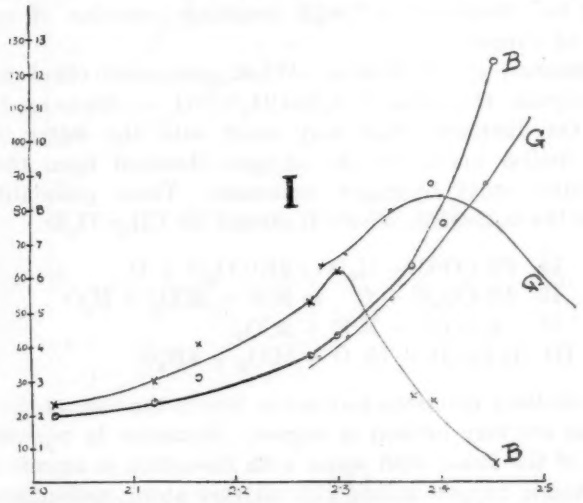
$c.$	ϵ_H.	CO_2.	O_2.
4·3	2·28	0·05	0·8
7·0	2·52	0·07	1·4
10·5	2·77	0·1	2·0
14·0	2·88	0·1	2·7
20	3·12	0·2	3·7
24	3·28	0·2	4·7
30	3·57	0·2	6·1
32	4·24	0·2	6·2
32	4·43	0·3	6·5
35	5·01	0·3	6·8
111	6·22	1·0	21·4
133	6·31	1·3	24·9
158	6·52	1·8	30·9
240	6·76	2·2	44·9

* The gold electrodes even under low potentials soon became coated with a brown covering of dispersed gold. The current and potential readings, however, were quite as constant as in the case of platinum, so it may be assumed that in spite of this "spattering" the surface area remained practically constant throughout.

This type of curve was also given when potassium trichloroacetate was used as electrolyte. With potassium ethyl malonate, however, a curve similar in all respects to that of Fig. 1 was obtained. The difference is therefore connected with the nature of the reactions at the anode and may be conditioned by the presence or

absence of halogen. Gibson assumes that the anode changes from "platinum α," which is stable at low potentials and which does not favour synthesis, to "platinum β," stable above 2·2 volts and favouring synthesis. The following facts would seem to lend support to this view. After a solution of potassium ethyl malonate had been electrolysed for a time at an anode potential above the synthetic value the applied *E.M.F.* was reduced so as to bring the anode potential below this value; the resulting current always approximated after a short interval to that obtained when ascending the curve. This was not the case when potassium trichloro-

FIG. 1.



Curve IB: *Bright platinum.* *Curve* IG: *Grey platinum.*

Horizontal axis: anode potential, ϵ_H. *in volts.*
Vertical axis: on left, current in milliamperes ⊙; *on right, oxygen per hour in c.c.* ×.

acetate was the electrolyte. For instance, a solution of the latter was electrolysed for 20 hours at a high potential. The anode potential was then 2·8 volts and the current 0·3 m.a. The applied *E.M.F.* was then reduced, the anode potential becoming 2·2 volts and the current 0·07 m.a. On the ascending curves the current corresponding to this potential was 0·65 m.a., nearly ten times as large. The anode was still covered with the large bubbles typical of synthesis, although the potential was now well below the synthetic potential. On removing these bubbles by rubbing with a piece of wire (without interruption of the current), although there was a momentary rise of current, it subsequently returned

rapidly to 0·07 m.a. as large bubbles reformed on the anode. Repeated rubbings effected no permanent change. The electrolysis was then allowed to proceed undisturbed for 5 days with the same constant applied *E.M.F.* At the end of this time, anode potential was still 2·2 volts, but the current had increased to 0·7 m.a., a value agreeing well with the 0·65 m.a. obtained in the ascending series. On Gibson's hypothesis, these results are simply explained by assuming that " platinum β " was formed on the surface of the anode during its period of high potential, that this " platinum β " continued to function as a synthetic agent on reduction of the potential below the normal synthetic value, but after the lapse of sufficient time it, being metastable at low potentials, had gradually reverted to " platinum α " with resulting cessation of synthesis and rise of current.

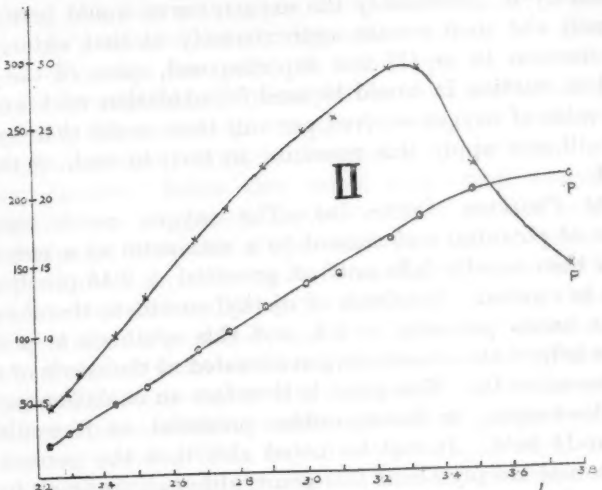
Interpretation of the Results.—When potassium ethyl malonate is electrolysed, the anion $CO_2Et{\cdot}CH_2{\cdot}CO{\cdot}O'$ is discharged at the anode. On discharge, this may react with the water, or with another similar anion, or the oxygen liberated from the water may oxidise ethyl hydrogen malonate. These possibilities are shown in the equations, where R stands for $CH_2{\cdot}CO_2Et$.

$$\text{Ia. } 2R{\cdot}CO{\cdot}O + H_2O = 2R{\cdot}CO_2H + O.$$
$$\text{Ib. } 2R{\cdot}CO_2H + O = R{\cdot}R + 2CO_2 + H_2O.$$
$$\text{II. } 2R{\cdot}CO{\cdot}O = R{\cdot}R + 2CO_2.$$
$$\text{III. } R{\cdot}CO_2H + 10\ O = 5CO_2 + 4H_2O.$$

Other subsidiary reactions may occur, but in the case of the malonates these are very limited in degree. Equation Ia represents the reaction of the anion with water with liberation of atomic oxygen. If this atomic oxygen unites with another atom, molecular oxygen is produced and escapes as gas at the anode. An equivalent quantity of hydrogen will be produced at the cathode by the reaction of the potassium ions, and the whole therefore amounts to the simple electrolysis of water. Equation Ib represents the formation of diethyl succinate as a result of the oxidation of the ethyl hydrogen malonate formed at the anode by the atomic oxygen simultaneously liberated. Equation II represents two discharged anions as uniting to form the same product, a molecule of carbon dioxide splitting off from each of them. Equation III represents complete oxidation of hydrogen ethyl malonate to carbon dioxide and water. It remains to determine which reactions prevail with the different electrodes and with different potentials. In general, equation Ia represents the prevailing reaction at low potentials. It would appear justifiable to look on this reaction as being maintained during rise of potential and to consider reaction Ib, II,

or III as being superimposed on it (compare Gibson, *loc. cit.*, p. 482).

FIG. 2.



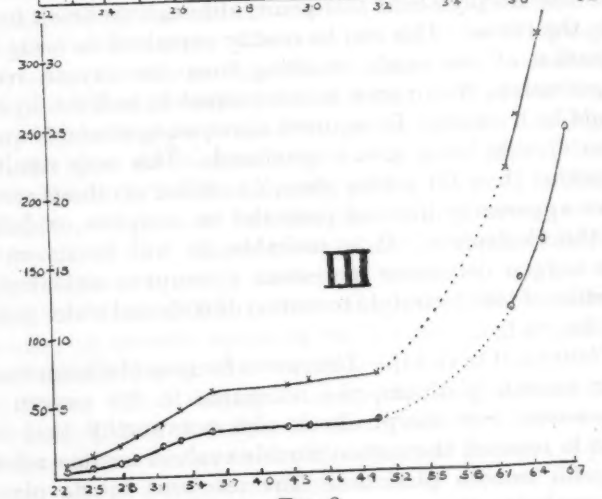


FIG. 3.

Curve II: *Platinised platinum.* *Curve* III: *Gold.*

Horizontal axis: anode potential, ϵ_H, *in volts.*

Vertical axis: on left, current in milliamperes ⊙; *on right, oxygen per hour in c.c.* ×.

There are then three possible forms of oxygen curve. (1) If reaction Ia alone holds throughout the whole range, the amount of oxygen evolved per unit time would be directly proportional to

the current, and would rise steadily with increasing potential, giving a continuously ascending curve. (2) If reaction II were superimposed at any stage, since no oxygen is either used up or produced by it, presumably the oxygen curve would here reach a maximum and then remain approximately at that value. (3) If either reaction Ib or III was superimposed, some of the oxygen formed in reaction Ia would be used for oxidation work and a fall in the value of oxygen evolved per unit time would thereby result.

We will now apply this reasoning in turn to each of the cases studied.

Bright Platinum (Curve Ib).—The oxygen curve rises with increase of potential and current to a maximum at a potential of 2·3 and then rapidly falls until at potential = 2·45 practically no oxygen is evolved. Synthesis of diethyl succinate therefore takes place at anode potential = 2·3, and this synthesis is performed with the help of the atomic oxygen liberated at the anode or according to equation Ib. This point is therefore an oxidation potential, not a discharging or decomposition potential, as it would be if equation II held. It will be noted also that the current curve begins to rise steeply about this point, although no break has been shown in the curve. This can be readily explained as being due to depolarisation of the anode resulting from the oxygen removal. At low potentials, the oxygen is never equal to half the hydrogen, as it would be if reaction Ia occurred alone, an appreciable quantity of carbon dioxide being always produced. This may result from either reaction Ib or III taking place, *i.e.*, either synthesis occurring below the apparently limiting potential or complete oxidation of part of the electrolyte. It is probable, as will be shown later, that the oxygen deficiency represents a complete oxidation of a small portion of the electrolyte to carbon dioxide and water (compare Murray, *loc. cit.*).

Grey Platinum (Curve Ig).—The curves for grey platinum resemble those for smooth platinum, the maximum in the oxygen curve being, however, less sharp. It is also noteworthy that before this point is reached the carbon dioxide evolved became relatively high as with smooth platinum. The reactions taking place are therefore probably the same in both cases. Although there is no direct experimental evidence to support the hypothesis, it seems probable that the comparative differences may be due to differences in surface current density.

Platinised Platinum (Curve II).—The oxygen and current curves rise steadily until an anode potential of about 3·3 is reached. The oxygen curve then falls while the current curve still ascends, although somewhat less steeply. If any synthesis takes place,

it is exceedingly small in amount, as is proved by the fact that on electrolysing 100 c.c. of solution between platinised platinum electrodes for 2 hours with a current of 2·5 amperes and extracting the resulting solution with ether, there remained on removal of the ether only a trace of an oily film which had not the characteristic odour of diethyl succinate. It would appear, therefore, that above an anode potential of 3·3 complete oxidation of the electrolyte (equation III) takes place in amount sufficient to produce a fall in the oxygen evolved. This is also shown by the larger increase in carbon dioxide. Below this value, only small quantities of carbon dioxide are produced, and relatively these are very much smaller compared with the oxygen evolved than is the case with smooth platinum. In order to test conclusively whether carbon dioxide is evolved at very low potentials, the following experiment was carried out. A modified apparatus was used which allowed a current of air free from carbon dioxide to be passed through the electrolyte. This was fitted with platinised electrodes and half filled with malonate solution to which a few drops of dilute sulphuric acid had been added. With no current passing, a slow stream of air was aspirated through the solution and then bubbled through a single drop of lime water contained in a small bubbling apparatus. After 2 hours there was no sign of milkiness in the lime water. This proved the malonate solution to be free from carbonate. A current of 10 milliamperes was then passed with an anode potential of 1·83, the same air current being continued. After ½ hour there was evidence of carbon dioxide and after 1 hour the milkiness was very definite. Oxidation was therefore taking place even at this very low potential. Since there is little doubt that the only oxidation occurring with platinised platinum is the complete oxidation of equation III, this would support the conclusion that in the case of smooth platinum the carbon dioxide produced at low potentials is due to this reaction.

Gold (Curve III).—With gold electrodes at low potentials there is a very small yield of carbon dioxide, but its presence was proved by an experiment similar to that described in the case of platinised platinum. It probably represents a small amount of complete oxidation. The oxygen evolved rises steadily till a potential of 3·6 is reached, then remains practically constant till potential = 5·0. Thereafter occurs a region of oscillating potentials. With an applied *E.M.F.* between the electrodes of 7·3 volts, the current varied during 12 hours between the limits of 40 and 8 milliamps., with corresponding anode potential variation of 5·0—6·0. Both rise and fall were very slow, each occupying from 1 to 2 hours, and they showed no diminution in magnitude with time. Above

potential = 6·2, rapidly ascending smooth curves are obtained. The carbon dioxide evolved remains very small throughout and even at the highest potential reached the oxygen deficiency is only about 10%. It would thus appear that with gold there is very little oxidation of any kind, the main reaction throughout being that of equation Ia. The peculiar nature of the curves between anode potentials of 3·6 and 6·2 is doubtless due to some form of electrode effect, most probably the formation of an oxide of gold. On this assumption one can imagine that at potential 3·6 the atomic oxygen liberated at the anode, instead of combining to form molecular oxygen, begins to combine with the gold. This tendency continues until potential = 5·0, the gradual reduction in conductivity of the electrode due to the formation of the film of oxide rendering this portion of the curve flat. Above this potential, *i.e.*, throughout the dotted portion of the curve where readings were not obtainable, the oxide film is alternately formed and destroyed as the potential varies between about 5·0 and 6·0, the lower potential favouring the formation of oxide and the higher one causing it to decompose with oxidation of the electrolyte. The variation in the conductivity of the electrode during these changes accounts for the changes in current, which throughout shows oscillations in an inverse direction to those of the potential. The final sharp rise in the curves represents a range where the oxide is either not formed or is destroyed as soon as formed and no polarising effect occurs.

Summary.

(1) The formation of diethyl succinate on electrolysis of potassium ethyl malonate is shown to be an oxidation reaction and to take place only when the anode is of a suitable material and when its potential exceeds 2·3—2·4 volts referred to the normal hydrogen electrode as standard. The results are in general agreement with the views expressed by Gibson.

(2) Grey platinum resembles smooth platinum in its behaviour as electrode material.

(3) With platinised platinum and with gold anodes no synthesis occurs; but whereas the former at a potential of 3·3 causes a large oxidation of the electrolyte to carbon dioxide and water, with the latter little oxidation occurs even at potentials over 6.

(4) What appears to be complete oxidation of a portion of the electrolyte occurs with all the anode materials used, even at very low potentials. The extent of this oxidation is small with platinised platinum and gold, more considerable with smooth platinum and grey platinum.

(5) With gold a peculiar instability is observed, and an explanation of this is suggested.

My thanks are due to Professor Sir James Walker, F.R.S., for suggesting the lines of this research, and for helpful criticism during its performance.

CHEMICAL DEPARTMENT,
UNIVERSITY OF EDINBURGH. [*Received, June 6th,* 1925.]

CCLXXXII.—*The Reaction of Bromine with Aliphatic Acids. Catalytic Effect of Acyl Halides.*

By HERBERT BEN WATSON.

THE investigation of the mechanism of the α-bromination of aliphatic acids originated in the isolation by Steiner (*Ber.*, 1874, **7**, 184) of a red additive compound of acetic acid, bromine, and hydrogen bromide, which decomposed in absence of water to give hydrogen bromide and monobromoacetic acid, and the accelerating effect of hydrogen bromide was interpreted by Hell and Mühlhäuser (*Ber.*, 1879, **12**, 727) on the hypothesis that bromination was preceded by the formation of a compound of this type. Hell and Urech (*Ber.*, 1880, **13**, 531) showed that, although the velocity of bromination is dependent on the concentration of bromine, the reaction is not of the simple bimolecular type, an initial period of very low velocity being followed by a comparatively rapid disappearance of the halogen; and they regarded this observation as confirmation of Hell and Mühlhäuser's hypothesis.

The rapid bromination of aliphatic acids in presence of phosphorus or sulphur (Hell, *Ber.*, 1881, **14**, 891; Volhard, *Annalen*, 1888, **242**, 141; Zelinsky, *Ber.*, 1887, **20**, 2026) was regarded originally as involving complete conversion of the acid into acid bromide, followed by bromination of the latter, but this interpretation is not applicable to cases where a very marked acceleration results from the presence of quantities of phosphorus or sulphur which are insufficient for any large conversion (*e.g.*, Gorodetzky and Hell, *Ber.*, 1888, **21**, 1729; Ward, J., 1922, **121**, 1161).

A new view of the reaction was put forward by Lapworth (J., 1904, **85**, 41). He observed that hydrogen chloride, as well as hydrogen bromide, has a catalytic effect, and he regarded this action as being of the same nature as the influence of acids on keto-enol changes; accordingly, he suggested that the bromination of carboxylic acids, like that of acetone, involves a relatively slow catalysed change to the enolic form, followed by instantaneous addition of

bromine at the point of unsaturation, and finally by loss of hydrogen bromide.

$$R\cdot CH_2\cdot CO_2H \xrightarrow{\text{catalyst}} R\cdot CH{:}C\begin{matrix}OH\\OH\end{matrix} \xrightarrow{Br_2} R\cdot CHBr\cdot C\begin{matrix}Br\\OH\\OH\end{matrix} \longrightarrow$$

$$R\cdot CHBr\cdot CO_2H + HBr.$$

He attributed the catalytic influence of *small* quantities of phosphorus to the formation of hydrogen bromide by the action of the phosphorus bromides on traces of water present or on the acid itself. This " enolic form theory " was adopted by Aschan (*Ber.*, 1912, **45**, 1913) to explain the production of brominated acid bromide and brominated acid chloride when bromine reacts with an acid chloride: but Meyer (*Ber.*, 1912, **45**, 2868) pointed out that such an interpretation is unnecessary, since the observation is explained equally well by assuming substitution followed by a reaction of hydrogen bromide with the brominated acid chloride (compare Staudinger and Anthes, *Ber.*, 1913, **46**, 1417). The results of an investigation of the bromination of acids in presence of small quantities of phosphorus were interpreted by Ward (*loc. cit.*) on the basis of Lapworth's suggestion, but he points out (J., 1923, **123**, 2212) that the theory demands the existence of carboxylic acids in a form which is neither observed nor indicated in other reactions: in the case of ketones, aldehydes, and compounds containing the $-CO\cdot CH_2\cdot CO-$ grouping where the theory has been applied successfully (Lapworth, J., 1904, **85**, 30; Dawson and Leslie, J., 1909, **95**, 1880; Dawson, Burton, and Ark, J., 1914, **105**, 1275; Meyer, *Annalen*, 1911, **380**, 235; *Ber.*, 1912, **45**, 2867; West, J., 1924, **125**, 1277), the existence of an enolide is indicated in other reactions.

The very powerful accelerating effect of a small quantity of acetic anhydride on the chlorination of acetic acid was observed by Hentschel (*Ber.*, 1884, **17**, 1286), and is now utilised in the industrial preparation of monochloroacetic acid. Hentschel postulated a pair of alternating reactions of the following type,

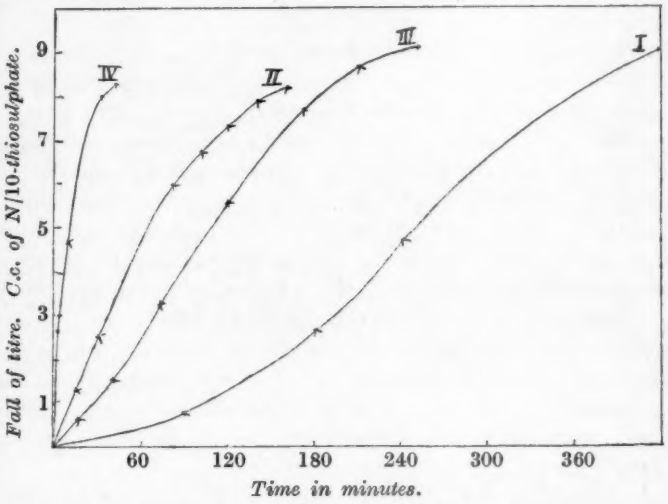
$$(CH_3\cdot CO)_2O + Cl_2 = CH_2Cl\cdot CO_2H + CH_3\cdot COCl \quad . \quad . \quad . \quad . \quad (1)$$

$$CH_3\cdot COCl + CH_3\cdot CO_2H = (CH_3\cdot CO)_2O + HCl \quad . \quad . \quad . \quad . \quad (2)$$

The individual reactions (1) and (2) had been observed by Gal (*Ann. Chim. Phys.*, 1869, **66**, 187) and Anschütz (*Annalen*, 1884, **226**, 1). Shaw (J., 1923, **123**, 2233) found that acetic anhydride similarly accelerates the bromination of acetic and homologous acids, and suggested that bromination may take place either (*a*) through the preliminary enolisation of the acid, or (*b*) through a series of changes involving acetic anhydride, similar to those postulated by Hentschel, the latter course being by far the more rapid.

A re-examination of the action of bromine on acetic, propionic, and *n*-butyric acids at 100° has been undertaken by the author, and the results are summarised in the following.

(a) *Catalytic Effect on Halogen Acids.*—When no catalyst is present initially, the course of the reaction indicates autocatalysis by the hydrogen bromide formed (see curve I): a "period of acceleration" is followed by the attainment of a maximum velocity, and the reaction then becomes steadily slower: variation in the initial concentration of bromine has a marked effect (compare Hell and Urech, *loc. cit.*). If hydrogen bromide is present initially, the



Acetic acid and bromine. Initial $[Br_2] = 0{\cdot}24\,M$.

I. *No added catalyst.* II. HBr *introduced* (0·268 *M*).
III. HCl *introduced* (0·317 *M*). IV. AcBr *introduced* (0·047 *M*).

reaction proceeds more quickly: a very small quantity of the halogen acid reduces the period of acceleration to a marked extent, and in presence of a moderate initial concentration of hydrogen bromide (0·2*M*) this period disappears (see curve II). The velocity is thus dependent on the concentration of bromine and that of hydrogen bromide: no simple mathematical relationship has been found for acetic and *n*-butyric acids, but in the case of propionic acid, when the acid is present in large excess, the velocity is represented with a tolerable degree of accuracy by the expression $v = k[Br_2][HBr]^{\frac{1}{2}}$. This expression holds over a wide range of concentration of hydrogen bromide extending from zero to molar (see Table II): when, however, the concentration of the halogen acid is very great (2*M*), a retarding influence comes into play.

This is undoubtedly due to perbromide formation, as indicated by the pale colour of the reaction mixture (compare Joseph and Jinendradasa, J., 1911, **99**, 274), a similar retardation having been observed in other reactions (Bugarsky, *Z. physikal. Chem.*, 1901, **38**, 561; 1904, **48**, 63; Bognar, *ibid.*, 1910, **71**, 529; Orton and Jones, *Rep. Brit. Assoc.*, 1910, 99). Hydrogen chloride also exerts a catalytic effect (compare Lapworth, Shaw), but is somewhat less effective than hydrogen bromide, and when it is present even at saturation the initial period of acceleration does not disappear completely (see curve III). The velocity does not remain constant as stated by Shaw (*loc. cit.*), who apparently took an insufficient number of points on the curve.

In order to determine whether this catalytic action is common to all acids, the effect of small quantities of trichloroacetic and sulphuric acids was examined. The effect of trichloroacetic acid is scarcely perceptible (see Table 1, *a* and *b*): sulphuric acid also has but little effect, but the bromination is here complicated by side reactions. The marked catalytic effect of halogen acids is clearly specific, and not common to acids in general, and this fact together with the dependence of the velocity on the concentration of bromine is evidence against the validity of the "enolic form theory."

(b) *Catalytic Effect of Acetyl Bromide.*—The very powerful acceleration produced by the presence of a small quantity of acetic anhydride was observed by Shaw (*loc. cit.*), and a fuller investigation of this reaction at 100° has established the following facts (the acetic acid used contained 0·1% of water, and in all cases was present in very great excess):

(1) If the anhydride is not in excess of the water present in the acid, no catalytic effect is observed.

(2) When the anhydride is in excess of the water, a short period of acceleration (which escaped Shaw's notice) is followed by a rapid reaction: after the initial period, the velocity is proportional to the concentration of bromine, and varies directly and almost proportionately with that of the anhydride (see Tables IV and V). The effect of acetic anhydride, as compared with that of halogen acids, is seen from the following:

Catalyst added.	No catalyst.	HBr = 0·053*M*.	HCl = 0·063*M*.	Ac_2O = 0·05*M*.
Initial titre ($N/10$-$Na_2S_2O_3$) ...	9·48	9·58	10·02	9·25
Fall of titre in 45 mins.	0·25	1·55	0·78	9·05

(3) If hydrogen bromide, in excess of the anhydride, is also introduced, the initial period of acceleration disappears, and the velocity is proportional to the concentration of bromine from the commencement. The actual value of k_1 is somewhat smaller than in (2), and

becomes very considerably smaller when the concentration of hydrogen bromide is high (see Table VI). This may be attributed to perbromide formation, which is indicated by the colour of the reaction mixture : such combination becomes more extensive as the water content of acetic acid diminishes (Jones, J., 1911, **99**, 402). A slight falling off in the value of k_1 towards the end of the reaction, which was observed in some of the experiments, is probably due to the same cause.

(4) The presence of hydrogen chloride in excess of the anhydride does not destroy the catalytic effect of the latter, as stated by Shaw (*loc. cit.*), but exerts a comparatively small retarding influence. Here again, after the initial period, the velocity is proportional to the concentration of bromine (see Table VII).

It is suggested that these results are best interpreted as follows : when a mixture of acetic acid, bromine, and acetic anhydride is heated at 100°, the anhydride not being in excess of the water present in the acid, complete and relatively instantaneous hydrolysis of the anhydride takes place, and no acceleration is observed. If the anhydride be in excess of the water, the first reaction consists in an immediate removal of water by hydrolysis of the equivalent quantity of anhydride. The remainder then reacts with bromine, $(CH_3{\cdot}CO)_2O + Br_2 = CH_2Br{\cdot}CO_2H + CH_3{\cdot}COBr$ (Gal, *loc. cit.*) : with the quantities of anhydride employed in the investigation, the percentage of the total bromine required for this reaction is small, being equivalent to about 0·5 c.c. of N/10-thiosulphate. The conclusion is thus reached that the observed acceleration is due to the presence of acetyl bromide. If this be the case, the velocity will reach its maximum value only when the bromination of the anhydride is complete, and thus the period of acceleration is accounted for. In presence of the more powerful catalyst the influence of the hydrogen bromide formed is inappreciable (or perhaps is balanced by perbromide formation), and there is no apparent autocatalysis : the reaction therefore follows the first order. If hydrogen bromide is present initially in excess of the anhydride, it reacts with great speed according to the equation $(CH_3{\cdot}CO)_2O + HBr = CH_3{\cdot}CO_2H + CH_3{\cdot}COBr$ (compare Gal, *loc. cit.*, on the reaction of hydrogen chloride with acetic anhydride). The acid bromide is then present from the commencement at its maximum concentration, and there is no period of acceleration.

In order to obtain direct evidence of the accelerating influence of acetyl bromide, the bromination of acetic acid in presence of varying small quantities of the acid bromide (introduced as such) was studied; the results confirmed the hypothesis outlined above (see Tables VIII and IX). When the acetyl bromide is not in

excess of the water present in the acid, the reaction follows, as would be expected, the same course as when hydrogen bromide alone is introduced, while the acid bromide, present in excess of the water, is an exceedingly powerful catalyst* (see curve IV). Its effect is similar to that of the anhydride at equivalent concentration save that (*a*) the velocity is now proportional to the concentration of bromine from the commencement, and (*b*) the values of k_1 are somewhat lower (perbromide formation), and in agreement with the values obtained in presence of acetic anhydride and hydrogen bromide in conjunction. Measurements employing varying initial quantities of the catalyst showed that the velocity is proportional to the concentration of acetyl bromide (see Table X).

Acetyl bromide exerts a similar influence on the bromination of other aliphatic acids. The effect of acetic anhydride on the bromination of the homologues of acetic acid was observed by Shaw (*loc. cit.*), and the author has shown that acetic anhydride and acetyl bromide accelerate the bromination of propionic and *n*-butyric acids in a manner exactly similar to that described for acetic acid.

Examination of the effect of acetyl chloride has shown that if the acid chloride is not in excess of the water present it produces the same effect as does hydrogen chloride, while if it is in excess of the water the bromination is initially much faster than in presence of halogen acids, but less rapid than in presence of acetyl bromide: when sufficient hydrogen bromide has been produced to bring about complete conversion of the acid chloride to acid bromide ($CH_3{\cdot}COCl + HBr \rightleftarrows CH_3{\cdot}COBr + HCl$, Staudinger and Anthes, *loc. cit.*) a rapid first-order reaction takes place: the actual value of k_1 is the same as when acetic anhydride is initially present and somewhat greater than when acetyl bromide is introduced initially (less " fixing " of bromine as perbromide). Acetyl chloride is thus a less powerful catalyst than acetyl bromide. The retarding in-

* An anomalous result obtained by Ward (J., 1922, **121**, 1164) receives a simple interpretation in the light of this fact. He found that acetic acid, previously saturated with hydrogen bromide, did not react completely with a molecular proportion of bromine after heating at 100° for *three* hours, and this observation is in harmony with the results of Lapworth (*loc. cit.*) and of the author. On the other hand, when he introduced acetyl bromide for the purpose of dehydrating the acid and at the same time providing halogen acid, he carried out the bromination in *one* hour. The amount of acetyl bromide added (3 g. to 50 g. of acetic acid) was equivalent to the water content of an acid having 0·878% of water (m. p. rather above 15°). Ward's acid had been purified by freezing, and it is unlikely that it contained such a high percentage of water. The indications are that the acetyl bromide was in excess of the water, and that its presence was responsible for the rapid bromination.

fluence of an excess of hydrogen chloride on the bromination in presence of acetic anhydride may then be attributed to the formation of acid chloride from the anhydride $(CH_3{\cdot}CO)_2O + HCl = CH_3{\cdot}CO_2H + CH_3{\cdot}COCl$ (Gal, *loc. cit.*); complete conversion of acid chloride into acid bromide during the reaction is here prevented by the excess of hydrogen chloride, and hence the comparatively small value of k_1.

(c) *Catalytic Effect of Acid Bromides in General.*—Investigation of the bromination of acetic and propionic acids in presence of bromoacetyl, propionyl, and benzoyl bromides has revealed the fact that the introduction of any one of these acid bromides brings about an acceleration identical with that which is produced by acetyl bromide at equivalent concentration. The velocity is proportional to the concentration of bromine and of acid bromide, and the values of k_1 are the same in each case (see Tables X and XI).

The introduction of benzoyl chloride into a reaction mixture of bromine and acetic acid produces an effect which is similar to that of acetyl chloride at equivalent concentration, except that the velocity is slightly less (see Table XII).

Discussion of Results.

1. The peculiar catalytic influence of *acid bromides* on the bromination of aliphatic acids may possibly involve the following steps. The acid bromide is first brominated,

$$R{\cdot}CH_2{\cdot}COBr + Br_2 = R{\cdot}CHBr{\cdot}COBr + HBr \quad . \quad . \quad . \quad (1)$$

The aliphatic acid (present in very great excess) then reacts with the brominated acid bromide,

$$R{\cdot}CHBr{\cdot}COBr + R{\cdot}CH_2{\cdot}CO_2H = R{\cdot}CH_2{\cdot}COBr + R{\cdot}CHBr{\cdot}CO_2H \quad (2)$$

the final product being the brominated acid, and the acyl bromide going through the same series of changes again.

The results of Urech (*Ber.*, 1880, **13**, 1688) indicate that the bromination of acetyl bromide is a reaction of the second order; in the scheme outlined above, the concentrations of acid bromide and brominated acid bromide remain constant during the reaction, while that of the acid is very large; for a given initial concentration of acid bromide, therefore, the velocity will vary only as the concentration of bromine, but will be proportional to the initial concentration of acid bromide. This is in complete agreement with the observed facts.

If the bromide of a different carboxylic acid be present initially, an exactly similar acceleration is observed, and a similar mechanism is thus indicated. This is interpreted most simply by supposing that reactions (1) and (2) above are preceded by

$$R'{\cdot}COBr + R{\cdot}CH_2{\cdot}CO_2H = R{\cdot}CH_2{\cdot}COBr + R'{\cdot}CO_2H,$$

which is exactly similar in character to reaction (2). This idea is in harmony with the observation of Polzenius (*Chem. Ztg.*, 1896, **20**, 46) that benzoyl chloride and acetic acid when heated together yield benzoic acid and acetyl chloride, whilst a similar reaction was suggested by Orton (J., 1901, **79**, **1351**) as providing a possible explanation of the formation of acid amides by the reaction of benzoyl chloride with carboxylic acids in presence of ammonia.

The catalytic action of acid bromides cannot be interpreted by postulating the intermediate formation of the acid anhydride (compare Shaw, *loc. cit.*) or of a mixed anhydride, for an initial period of low velocity is observed when the anhydride is introduced, but not when the acid bromide is present initially.

2. *Acid chlorides* are less powerful catalysts than acid bromides, but their effect may be interpreted in a similar manner by postulating the reactions

$$R'\cdot COCl + R\cdot CH_2\cdot CO_2H = R\cdot CH_2\cdot COCl + R'\cdot CO_2H,$$
$$R\cdot CH_2\cdot COCl + Br_2 = R\cdot CHBr\cdot COCl + HBr,$$
$$R\cdot CHBr\cdot COCl + R\cdot CH_2\cdot CO_2H = R\cdot CH_2\cdot COCl + R\cdot CHBr\cdot CO_2H.$$

It must be assumed that one or more of these reactions proceed less rapidly than the corresponding reactions involving the acid bromide. The hydrogen bromide formed in the reaction, however, now reacts with the acid chloride (or brominated acid chloride), and the above reactions are gradually replaced by those in which the acid bromide takes part (compare Staudinger and Anthes, *loc. cit.*). The velocity ultimately attained will depend on the proportion of acid bromide or brominated acid bromide present in the equilibrium $R\cdot CH_2\cdot COCl + HBr \rightleftharpoons R\cdot CH_2\cdot COBr + HCl$ or the equilibrium $R\cdot CHBr\cdot COCl + HBr \rightleftharpoons R\cdot CHBr\cdot COBr + HCl$, and is not likely to be identical for all acid chlorides. This is in harmony with experimental results.

3. The accelerating effect of a small amount of *phosphorus* (Hell-Volhard-Zelinsky reaction) is now interpreted simply. The bromination of acetic acid at 100° in presence of a halogen acid is a slow process requiring at least *six* hours for completion (Lapworth, Ward; compare the author's results, Tables I to III), whilst in presence of a very small amount of phosphorus the reaction is complete in *one* hour (Ward, J., 1922, **121**, 1163). The catalytic effect of phosphorus is thus much more powerful than that of halogen acids, but is of the same order of magnitude as the effect of acid bromides. Moreover, the bromination in presence of phosphorus always results in the formation of a small quantity at least of acid bromide or brominated acid bromide (Ward), and it seems obvious that the acceleration is to be attributed to this small quantity of acid bromide.

4. *Halogen acids.* It may be further suggested that the effect of halogen acids is due to traces of the acid halides present in equilibrium with the aliphatic acid, $R{\cdot}CO_2H + HX \rightleftharpoons R{\cdot}COX + H_2O$. The very different effects of halogen acids and acyl halides indicate that the quantity of acyl halide necessary to produce the observed velocity would be too small for detection, and the existence of such an equilibrium has never been demonstrated. It is not impossible, however, in view of the reversible nature of the hydrolysis of many inorganic chlorides, while it is suggested by reactions of the type $R{\cdot}CN + R'{\cdot}CO_2H + 2HCl = R{\cdot}CO{\cdot}NH_2,HCl + R'{\cdot}COCl$ (Colson, *Compt. rend.*, 1895, **121**, 1155). An interpretation of this type is supported by the following facts: (*a*) the influence of halogen acids is specific, and not common to acids in general; (*b*) Lapworth (J., 1904, **85**, 41) observed that a small quantity of water (which would displace the above equilibrium towards the left-hand side, thus reducing the concentration of acyl halide) reduced very considerably the speed of bromination, and this result has been confirmed by the author; (*c*) when varying amounts of the acid bromide (producing the above equilibrium) are added, there is a continuous increase in velocity as the amount of acid bromide becomes greater, and not a sudden increase at the point where the bromide is just in excess of the water (see Table VIII), whilst, on the other hand, addition of anhydride causes a sudden increase at this point (see Table IV); in the former case, therefore, a gradual increase in the amount rather than a sudden change in the nature of the catalyst is indicated.

The above suggestion, by postulating a similar mechanism in every case, brings into harmony all previous observations of the catalysed bromination of aliphatic acids.

In ascribing the rapid bromination to an initial interaction of bromine with the acyl bromide, no hypothesis is at present put forward as to the stages of this reaction, but it is possible that the acyl bromide "enolises" or passes into an "active" state more readily and rapidly than the acid. In that case, the reaction would be the result of a *rapid* enolisation followed by a *slow* reaction with bromine,

$$R{\cdot}CH_2{\cdot}COBr \xrightarrow{\text{rapid}} R{\cdot}CH{:}C\begin{matrix}OH\\Br\end{matrix} \xrightarrow[Br_2]{\text{slow}} R{\cdot}CHBr{\cdot}C\begin{matrix}Br\\Br\\OH\end{matrix} \xrightarrow{\text{rapid}} R{\cdot}CHBr{\cdot}COBr + HBr$$

(compare West, J., 1924, **125**, 1282). In such a suggestion α-bromination finds an easy explanation.

Experimental.

The acetic acid used throughout the investigation, except where otherwise indicated, melted at 16·4° (H_2O = 0·1%). All specimens of Kahlbaum's "100% acetic acid" examined were completely free from impurities which react with bromine at the ordinary temperature: in some cases, this acid melted at 16·4°, and was used without fractionation, while from specimens of lower melting point (16–16·2°) good yields of acid melting at 16·4° were obtained by fractional distillation through an eight-pear still-head. Post-war acetic acids of British manufacture which were not stable to bromine at the ordinary temperature were purified by distillation from chromic anhydride (Orton and Bradfield, J., 1924, **125**, 960) followed by fractionation. The propionic and *n*-butyric acids were prepared by distillation of "Kahlbaum" acid, the fractions used boiling respectively at 140·8—141°/764 mm. and 162·2—162·3°/766 mm. Solutions of bromine in these acids showed no appreciable fall of thiosulphate titre after several days at 25°. The bromine was shaken three times with an equal volume of water, dried under concentrated sulphuric acid, and finally separated and distilled from a little barium carbonate in an all-glass apparatus.

The method employed in the velocity measurements was similar to that of Hell and Urech (*loc. cit.*) and of Shaw (*loc. cit.*). A reaction mixture was made up containing the aliphatic acid, bromine, and the catalyst in the desired proportions, the aliphatic acid always being in large excess. The thiosulphate titre of 2 c.c. was determined, and portions of 2 c.c. were then introduced into small tubes: the tubes were sealed immediately, and immersed in a bath of boiling water. At given intervals tubes were withdrawn, broken under aqueous potassium iodide, and the iodine was titrated against standard thiosulphate. The figures in the tables which follow refer to c.c. of *N*/10-thiosulphate: time is stated throughout in minutes.

Catalytic Effect of Halogen Acids.

Solutions of hydrogen bromide in the aliphatic acids were prepared by dropping aqueous hydrobromic acid (*d* 1·7) on to phosphorus pentoxide, and passing the evolved gas over moist red phosphorus, then over phosphorus pentoxide, and finally into the aliphatic acid. The solutions of hydrogen chloride were obtained by dropping pure concentrated hydrochloric acid into pure concentrated sulphuric acid, and passing the gas liberated over calcium chloride and then into the aliphatic acid. The concentrations of the solutions were determined by precipitation as silver bromide or chloride, and the required volumes were introduced into different reaction mixtures.

TABLE I.

Acetic Acid and Bromine.

(*a*) No added catalyst.

I.		II.		III.	
Time.	Titre.	Time.	Titre.	Time.	Titre.
0	18·70	0	9·48	0	5·20
60	18·15	90	8·68	60	4·62
120	17·35	180	6·82	120	3·75
210	14·55	240	4·75	240	1·22
270	10·00	270	3·48	300	0·48
330	6·35	300	2·85		
480	0·72	330	2·10		
		420	0·45		

(*b*) $CCl_3 \cdot CO_2H$ as catalyst.

$[CCl_3 \cdot CO_2H] = 0{\cdot}206M.$	
Time.	Titre.
0	9·40
90	8·25
180	5·90
210	4·95
240	3·60
270	2·65
300	1·88
360	0·82

(*c*) Hydrogen bromide as catalyst.

I. Initial [HBr] = 0·268*M*.		II. Initial [HBr] = 0·268*M*.		III. Initial [HBr] = 0·053*M*.	
Time.	Titre.	Time.	Titre.	Time.	Titre.
0	18·08	0	9·48	0	9·58
15	16·32	10	8·62	10	9·12
30	14·42	15	8·18	20	8·95
45	12·35	30	6·92	40	8·25
60	10·22	40	6·12	80	6·55
100	5·72	60	4·78	140	3·75
140	3·25	80	3·62	200	1·70
180	1·72	100	2·80	260	0·65
230	0·78	120	2·15		
		140	1·65		
		160	1·20		

(*d*) Hydrogen chloride as catalyst.

I. [HCl] = 0·317*M*.		II. [HCl] = 0·317*M*.		III. [HCl] = 0·063*M*.		IV. [HCl] = 1·78*M*.	
Time.	Titre.	Time.	Titre.	Time.	Titre.	Time.	Titre.
0	17·18	0	9·92	0	10·02	0	9·52
10	16·85	15	9·28	15	9·78	20	8·05
20	16·45	40	8·38	30	9·50	45	6·15
50	14·45	75	6·58	60	9·05	90	3·48
80	13·22	100	5·22	120	7·55	120	2·95
110	10·58	120	4·42			210	0·68
140	8·98	140	3·40				
250	2·55	170	2·20				
		210	1·28				
		250	0·70				

Effect of Acetic Anhydride.

Acetic Acid and Bromine.—(a) *Presence of acetic anhydride alone.* The acetic anhydride was purified by redistillation through an eight-pear still-head, as described by Orton and Jones (J., 1912, 101, 1720). Mixtures of acetic acid (m. p. 16·4°), bromine, and varying small quantities of the anhydride were made up, and the

Table II.

Propionic Acid and Bromine.

Values of k are calculated from the formula $v = k[Br_2][HBr]^{\frac{1}{2}}$. If a be the initial concentration of hydrogen bromide, and b the initial concentration of bromine, this becomes $v = k(b - x)(a + x)^{\frac{1}{2}}$, which on integration gives,

$$kt = \frac{1}{\sqrt{b+a}}\left[\log_e \frac{\sqrt{b+a}+\sqrt{a+x}}{\sqrt{b+a}-\sqrt{a+x}} - \log_e \frac{\sqrt{b+a}+\sqrt{a}}{\sqrt{b+a}-\sqrt{a}}\right].$$

(*a*) No added catalyst.

I.			II.		
Time.	Titre.	k.	Time.	Titre.	k.
0	16·70	—	0	9·85	—
64	15·78	0·0113	60	9·60	0·0116
150	14·32	0·0082	90	9·32	0·0105
210	12·92	0·0077	120	9·05	0·0093
270	9·70	0·0088	150	8·78	0·0104
300	7·98	0·0094	240	7·40	0·0092
360	4·28	0·0112	300	6·52	0·0089
420	2·62	0·0116	390	3·95	0·0106
480	1·12	0·0131	420	3·52	0·0106
			510	1·40	0·0128

(*b*) Hydrogen bromide as catalyst.

I. Initial [HBr] = 0·0442M.			II. Initial [HBr] = 0·4455M.		
Time.	Titre.	k.	Time.	Titre.	k.
0	10·22	—	0	11·18	—
28	9·55	0·0107	15	9·95	0·0107
90	8·35	0·0087	30	8·65	0·0119
215	4·55	0·0112	45	7·45	0·0126
270	2·68	0·0132	60	6·42	0·0128
330	1·20	0·0143	75	5·28	0·0137
			90	4·38	0·0140
			105	3·70	0·0140
			125	2·68	0·0150

III. Initial [HBr] = 0·8908M.			IV. Initial [HBr] = 2·21M.		
0	11·00	—	0	10·75	—
15	9·65	0·0092	33	8·30	0·0052
30	8·32	0·0096	84	5·35	0·0056
45	6·95	0·0105	210	1·75	0·0059
60	5·80	0·0107			
75	4·98	0·0107			
90	4·00	0·0115			
120	2·80	0·0111			
150	1·75	0·0094			
180	1·25	0·0114			

course of the bromination was followed as described above. In two experiments the anhydride was insufficient to react with the whole of the water present in the acid, whilst in the remaining three it was in excess. The results obtained are indicated in Tables IV and V.

Table III.

n-Butyric Acid and Bromine.

(*a*) No added catalyst. (*b*) Hydrogen bromide as catalyst.

		I. Initial [HBr] = 0·2738*M*.		II. Initial [HBr] = 0·8215*M*.	
Time.	Titre.	Time.	Titre.	Time.	Titre.
0	9·28	0	10·28	0	9·48
60	8·12	15	9·75	10	8·98
180	5·45	30	9·25	20	8·35
240	4·30	60	8·25	30	7·85
300	3·82	120	6·32	60	6·38
360	2·75	240	3·05	90	5·15
420	1·65	390	0·92	120	4·02
				150	3·25
				180	2·45

Table IV.

	A.	B.	C.	D.	E.	F.
Grams Ac_2O added in 25 c.c.	0	0·0558	0·1104	0·1637	0·2334	0·2732
% water remaining after hydrolysis of Ac_2O	0·10	0·062	0·025	0	0	0
Conc. of Ac_2O in excess of water	0	0	0	0·007	0·03	0·05*M*
Initial titre (N/10-$Na_2S_2O_3$)	9·48	9·42	9·45	9·45	9·45	9·25
Fall of titre in 20 mins.	0·05	0·15	0·20	1·50	4·03	6·97
Fall of titre in 45 mins.	0·25	0·45	0·48	5·90	8·15	9·05

Table V.

Values of $k_1 = \frac{1}{t_2 - t_1} \cdot \log_e \frac{a - x_1}{a - x_2}$ for reactions E and F above.

E. $[Ac_2O] = 0·03M$. $t_1 = 15$.			F. $[Ac_2O] = 0·05M$. $t_1 = 10$.			F′. $[Ac_2O] = 0·05M$. $t_1 = 10$.		
Time.	Titre.	k_1.	Time.	Titre.	k_1.	Time.	Titre.	k_1.
0	9·45		0	9·25		0	13·75	
5	9·25		5	9·15		5	13·40	
10	8·62		10	6·98		10	9·92	
15	7·08		15	4·20	0·101	15	5·20	0·129
20	5·42	0·053	20	2·28	0·112	20	3·05	0·118
25	3·98	0·057	25	1·42	0·106	25	2·05	0·104
30	3·32	0·051	30	0·85	0·106	30	1·35	0·100
35	2·28	0·056	35	0·58	0·100	40	0·65	0·091
40	1·75	0·055						
45	1·30	0·056						
55	1·02	0·048						
	Mean	0·054		Mean	0·105		Mean	0·108

(b) *Presence of acetic anhydride and hydrogen bromide in conjunction.*

TABLE VI.

$[Ac_2O] = 0{\cdot}05M$. (Compare F and F', Table V.)

Values of $k_1 = 1/t \,.\, \log_e a/a - x$.

I. $[HBr] = 0{\cdot}1065M$.			II. $[HBr] = 0{\cdot}2683M$.			III. $[HBr] = 1{\cdot}3M$.		
Time.	Titre.	k_1.	Time.	Titre.	k_1.	Time.	Titre.	k_1.
0	13·68		0	13·40		0	13·95	
5	8·98	0·076	15	5·15	0·064	10	12·12	0·014
7	8·15	0·074	25	2·95	0·060	20	10·10	0·016
10	6·25	0·078	35	1·78	0·057	30	8·62	0·016
15	4·32	0·077	45	1·10	0·056	50	6·05	0·017
30	1·65	0·074	55	0·70	0·054	90	3·15	0·016
50	0·58	0·063						
	Mean	0·073		Mean	0·058		Mean	0·016

(c) *Presence of acetic anhydride and hydrogen chloride in conjunction.*

TABLE VII.

$[Ac_2O] = 0{\cdot}05M$. (Compare F and F', Table V.)

Values of $k_1 = \dfrac{t}{t_2 - t_1} \,.\, \log_e \dfrac{a - x_1}{a - x_2}$. $t_1 = 10$ mins.

I. $[HCl] = 0{\cdot}317M$.			II. $[HCl] = 1{\cdot}57M$.		
Time.	Titre.	k_1.	Time.	Titre.	k_1.
0	13·35		0	14·20	
5	12·38		5	12·40	
10	10·48		10	10·55	
15	8·25	0·047	20	6·92	0·042
20	6·25	0·051	30	4·48	0·043
30	3·80	0·051	45	2·10	0·046
	Mean	0·050		Mean	0·044

Effect of Acetyl Bromide.

The acetyl bromide was purified from dissolved halogen acid by bubbling dried air through the liquid under reduced pressure, and then fractionally distilled. Reaction mixtures of acetic acid, bromine, and varying small quantities of the acid bromide were made up and treated as before. The results are indicated in Tables VIII and IX.

TABLE VIII.

	A.	B.	C.	D.
Grams AcBr added in 25 c.c.	0·0892	0·1518	0·2157	0·3212
% water remaining after hydrolysis of AcBr	0·050	0·014	0	0
Conc. of AcBr in excess of water	0	0	trace	0·047
[HBr] formed by hydrolysis of AcBr ...	0·029M	0·049M	0·058M	0·058M
Initial titre ($N/10$-$Na_2S_2O_3$)	9·35	9·32	9·38	9·55
Fall of titre in 20 mins.	0·35	0·82	2·25	6·90
Fall of titre in 30 mins.	0·70	1·42	3·20	8·00

TABLE IX.

Values of $k_1 = 1/t \cdot \log a/a - x$ for reaction D above.

[AcBr] = 0·047*M*.

Time	0	5	8	10	15	20	30	
Titre	9·55	6·95	5·65	4·92	3·60	2·65	1·55	Mean
k_1 ...		0·064	0·064	0·066	0·065	0·063	0·061	0·064

Comparison of Effects of Different Acid Bromides.

Pure acetyl bromide was obtained as already described. Propionyl, benzoyl, and bromoacetyl bromides were prepared by treatment of propionic, benzoic, and acetic acids respectively with the required quantities of red phosphorus and bromine. The product was distilled from the phosphorus compounds under reduced pressure, and finally fractionated at ordinary pressure (compare Claisen, *Ber.*, 1881, **14**, 2473; Auwers and Bernhardt, *Ber.*, 1891, **24**, 2219). Reaction mixtures containing acetic or propionic acid (in large excess), bromine, and equivalent quantities of the different acid bromides were made up, and the reaction at 100° followed as before.

TABLE X.

Acetic Acid and Bromine.

M. p. of acetic acid 16·48° (% H_2O = 0·06).

Values of $k_1 = 1/t \cdot \log a/a - x$.

$CH_3 \cdot COBr$ = 0·0745*M*.			$CH_3 \cdot CH_2 \cdot COBr$ = 0·0745*M*.			$C_6H_5 \cdot COBr$ = 0·0745*M*.			$CH_2Br \cdot COBr$ = 0·0727*M*.		
Time.	Titre.	k_1.	Time.	Titre.	k_1.	Time.	Titre.	k_1.	Time.	Titre.	k_1
0	9·10		0	8·98		0	9·38		0	9·25	
3	6·92	0·092	3	6·88	0·089	3	7·00	0·098	3	7·18	0·085
6	4·95	0·101	6	4·75	0·105	6	4·78	0·112	6	5·25	0·094
9	3·68	0·100	9	3·40	0·107	9	3·52	0·109	9	3·82	0·098
12	2·88	0·096	12	2·58	0·104	12	2·68	0·104	12	2·95	0·095
15	2·15	0·096	15	1·92	0·102	15	2·15	0·098	15	2·35	0·091
20	1·38	0·094	20	1·22	0·100	20	1·35	0·097	20	1·62	0·087
25	0·95	0·089	25	0·75	0·099	25	0·92	0·092			
	Mean	0·096		Mean	0·101		Mean	0·101		Mean	0·092

$CH_3 \cdot COBr$ = 0·0527*M*.			$CH_3 \cdot CH_2 \cdot COBr$ = 0·0527*M*.			$C_6H_5 \cdot COBr$ = 0·0527*M*.		
Time.	Titre.	k_1.	Time.	Titre.	k_1.	Time.	Titre.	k_1.
0	9·35		0	8·05		0	9·18	
5	6·68	0·067	5	5·52	0·075	5	6·32	0·074
10	4·58	0·072	10	3·62	0·080	10	4·78	0·065
15	3·15	0·073	15	2·42	0·080	15	2·85	0·077
20	2·35	0·069	20	1·65	0·078	20	2·00	0·076
25	1·75	0·067	25	1·18	0·077	25	1·52	0·072
30	1·25	0·067	30	0·80	0·076	30	1·12	0·070
35	0·95	0·065	35	0·55	0·076	35	0·80	0·069
	Mean	0·069		Mean	0·077		Mean	0·072

Summary of Table X.

Catalyst.	C.	k_1.	k_1/C.	C.	k_1.	k_1/C.
$CH_3 \cdot COBr$	0·0745	0·096	1·29	0·0527	0·069	1·31
$CH_3 \cdot CH_2 \cdot COBr$	0·0745	0·101	1·35	0·0527	0·077	1·46
$C_6H_5 \cdot COBr$	0·0745	0·101	1·35	0·0527	0·072	1·37
$CH_2Br \cdot COBr$	0·0727	0·092	1·27			

Table XI.

Propionic Acid and Bromine.

Values of $k_1 = 1/t \cdot \log_e a/a - x$.

Equivalent quantities of acid bromides present.

$CH_3 \cdot COBr$.			$CH_3 \cdot CH_2 \cdot COBr$.			$C_6H_5 \cdot COBr$.		
Time.	Titre.	k_1.	Time.	Titre.	k_1.	Time.	Titre.	k_1.
0	9·30		0	8·62		0	8·65	
5	7·95	0·032	10	6·52	0·028	5	7·22	0·036
10	7·20	0·026	15	5·75	0·027	10	6·38	0·031
15	6·20	0·027	20	4·82	0·029	15	5·15	0·034
25	4·72	0·027	25	4·32	0·028	20	4·65	0·031
45	2·18	0·032	30	3·72	0·028	30	3·40	0·031
			35	2·72	0·032			
	Mean	0·029		Mean	0·029		Mean	0·033

Comparison of Effects of Acetyl and Benzoyl Chlorides.

The acid chlorides were purified by fractional distillation, and the reaction of acetic acid and bromine in presence of equivalent quantities of each was followed as before. M. p. of acetic acid 16·4° ($H_2O = 0·1\%$).

Table XII.

Values of $k_1 = \frac{1}{t_2 - t_1} \cdot \log_e \frac{a - x_1}{a - x_2}$. $t_1 = 6$ mins.

$CH_3 \cdot COCl = 0·05M$.			$C_6H_5 \cdot COCl = 0·05M$.		
Time.	Titre.	k_1.	Time.	Titre.	k_1.
0	9·38		0	9·68	
3	8·62		3	9·35	
6	6·98		6	8·08	
9	5·05	0·108	9	6·18	0·088
12	3·58	0·111	12	4·82	0·086
15	2·58	0·111	15	3·50	0·092
20	1·50	0·110	20	2·08	0·096
25	0·98	0·105	25	1·38	0·092
30	0·62	0·101	30	0·92	0·090
	Mean	0·108		Mean	0·090

In conclusion, the author wishes to express his gratitude to Professor Orton, F.R.S., who suggested the subject, for his advice and criticism during the progress of the research. The expense of the research was in part defrayed by a grant from the Chemical Society Research Fund, for which the author desires to tender his thanks.

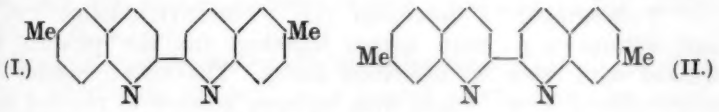
University College of North Wales,
Bangor.

[*Received, June 18th,* 1925].

CCLXXXIII.—*Homologues of 2 : 2′-Diquinolyl.*

By EDWARD JOHN VENN CONOLLY.

2 : 2′-DIQUINOLYL was prepared by Weidel (*Monatsh.*, 1881, **2**, 491; 1886, **7**, 327) by the action of sodium on quinoline, and its constitution proved by Weidel and Strache (*ibid.*, 1886, **7**, 306) from a study of its oxidation products. The preparation of homologues from 6-, 7-, and 8-methylquinolines is described below. During this work several instances of steric hindrance were observed. Thus, under the conditions stated below, good yields of the corresponding diquinolyls (I) and (II) were obtained from 6- and 7-methylquinolines, but the yield from 8-methylquinoline was very small; the substitution of potassium for sodium did not materially alter the results. The proximity of the methyl group to the nitrogen atom in the pyridine ring therefore seems to hinder the union of the two quinolyl nuclei. Also an ethiodide of 8 : 8′-dimethyl-2 : 2′-diquinolyl (III) could not be obtained even at 180°, possibly because the tertiary nitrogen atoms are practically "di-ortho-substituted."



While attempting to prove the constitution of the diquinolyls by a Fittig-Wurtz synthesis, the method of Tschitschibabin (*Ber.*, 1923, **56**, 1879) was used for the preparation of 6-methylcarbostyril.

EXPERIMENTAL.

6 : 6′-*Dimethyl*-2 : 2′-*diquinolyl* (I).—6-Methylquinoline (70 g.) and sodium (7 g.) in small pieces were heated together at about 100° during 2 hours and then at 150—160° during 7 to 8 hours. The dark brown, extremely viscous product, which solidified when cooled, was triturated with dry ether; sodium was removed by means of a fine sieve, and the ethereal solution filtered. The light brown residue of crude dimethyldiquinolyl (yield 37 g.) was extracted once with alcohol (100 c.c.), which removed most of the dark coloured impurities, and the light yellow residue was then repeatedly crystallised from benzene, until constant in melting point.

The ethereal filtrate obtained above was evaporated and the oily product distilled up to 160°/20 mm.; the dark red residue, which gradually solidified, when recrystallised from benzene gave a further small yield of the dimethyldiquinolyl.

6 : 6′-*Dimethyl*-2 : 2′-*diquinolyl* crystallises from benzene in small, colourless needles, m. p. 202·5—203° (Found: C, 84·6; H, 5·8; *M*, in camphor by Rast's method, 279. $C_{20}H_{16}N_2$ requires C, 84·5; H, 5·6%; *M*, 284). It is moderately soluble in acetone, alcohol, or light petroleum and very soluble in chloroform. It is readily soluble in hot benzene or toluene, less soluble in the cold.

The *hydrochloride* crystallises from hot water in very minute needles. The *picrate*, obtained from the base and picric acid in alcoholic solution, is practically insoluble in acetone, benzene, or chloroform, but fairly soluble in glacial acetic acid, from which it crystallises in small, yellow needles, m. p. 282—283° (decomp.). The *ethiodide*, $C_{20}H_{16}N_2,C_2H_5I$, prepared by heating the base with excess of ethyl iodide in a sealed tube at 150° for 1½ hours, crystallised from much alcohol in sparkling needles, m. p. 277—278° (decomp.; darkening at 275°) (Found: I, 28·2. $C_{20}H_{16}N_2,C_2H_5I$ requires I, 28·9%).

7 : 7′-*Dimethyl*-2 : 2′-*diquinolyl* (II).—7-Methylquinoline (38 g.) and sodium (4 g.) were heated together, and the product was treated with ether, as described above. The brown residue was recrystallised several times from aqueous acetone to remove tarry impurities and finally from carbon tetrachloride. 7 : 7′-*Dimethyl*-2 : 2′-*diquinolyl* was thus obtained in tufts of colourless needles, m. p. 208—209° (Found: C, 84·0; H, 5·8%). It is soluble in alcohol, acetone, chloroform, ethyl acetate, or carbon tetrachloride, but crystallises best from the last-named.

The *picrate* crystallises from alcohol in slender, yellow needles, m. p. 285—286° (decomp.; darkening at 284°). The *ethiodide*, obtained by heating the base with ethyl iodide at 130° in a sealed tube for 1 hour, crystallises from alcohol in clusters of golden-yellow needles, m. p. 274—275° (decomp.).

8 : 8′-*Dimethyl*-2 : 2′-*diquinolyl* (III).—8-Methylquinoline (50 g.) and sodium (4 g.) were heated together under the conditions previously described, but little, if any, diquinolyl was formed; the heating was therefore continued at 150—160° during a further 24 hours. The very viscous, dark brown mass was treated as in the previous cases, the ether evaporated, and the oily product distilled up to 160°/20 mm. The residue, which set to a hard, resinous mass when cold, was dissolved in acetone, and water added until a turbidity ensued; in the course of 3 or 4 days, crystals embedded in resinous matter separated. These were freed from resin

by washing them with acetone, crystallised again from acetone, and fractionally crystallised from carbon tetrachloride (yield very poor).

8 : 8′-*Dimethyl*-2 : 2′-*diquinolyl* forms tufts of colourless needles, m. p. 147—147·5° (Found : C, 84·0; H, 5·6%; *M*, in camphor, 290). It is soluble in benzene, chloroform, alcohol, or ethyl acetate, and crystallises readily from ethyl bromide or ethyl iodide.

The *picrate*, precipitated on mixing alcoholic solutions of the base and picric acid, crystallises from ethyl acetate in yellow needles, m. p. 264—265° after darkening at 258°.

2-*Hydroxy*-6-*methylquinoline*.—When an intimate mixture of finely powdered, freshly fused potassium hydroxide (40 g.) and 6-methylquinoline (44 g.) was heated at 250°, hydrogen was evolved in the theoretical quantity. The cooled reaction mixture was dissolved in water, the solution filtered if necessary, and the crude methylcarbostyril precipitated by the addition of dilute hydrochloric acid. Recrystallised from hot water, it formed long, yellow needles, m. p. 225—230°, and therefore was still impure. On heating at 12 mm., it began to sublime at 50° and passed over at 240—241°; the colourless distillate crystallised from alcohol in monoclinic prisms, m. p. 232—233° (Einhorn and Lauch, *Annalen*, 1888, **243**, 359, give m. p. 228°) (Found : C, 75·6; H, 5·7. Calc., C, 75·5; H, 5·7%).

2-*Bromo*-6-*methylquinoline*.—6-Methylcarbostyril (14 g.) and phosphorus tribromide (30 c.c.) were heated together on the water-bath during 3 hours and the solution was then gently boiled during a further ½ hour. The liquid was poured into water and the 2-bromo-6-methylquinoline distilled in steam; it separated from the distillate in long, colourless needles (yield 5·3 g.) and from alcohol in long, faintly yellow needles, m. p. 117—118° (Fischer and Guthmann, *J. pr. Chem.*, 1916, **93**, 378, give m. p. 126°) (Found : Br, 36·2. Calc., Br, 36·0%).

The *picrate*, obtained from boiling alcoholic solution, crystallised from alcohol in glistening, golden needles, m. p. 140·5°. The *ethiodide*, $C_{10}H_8NBr,C_2H_5I$, prepared by heating the base with excess of ethyl iodide in a sealed tube at 130° during 1 hour, crystallised from ethyl acetate in yellow prisms, m. p. 110—111°.

Attempts to synthesise 6 : 6′-dimethyl-2 : 2′-diquinolyl from 2-bromo-6-methylquinoline by the Fittig-Wurtz reaction and by the use of Grignard reagents were unsuccessful.

The author is indebted to Professor F. S. Kipping, F.R.S., for his interest in this work, and to the Department of Scientific and Industrial Research for a maintenance grant.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, June 24th*, 1925.]

CCLXXXIV.—*The Thermal Decomposition of Ozone.*

By ROBERT OWEN GRIFFITH and ANDREW MCKEOWN.

IN an investigation of the reaction between ozone and hydrogen at 100°, the results of which will shortly be published, it was necessary to compare the intrinsic rate of the reaction $2O_3 \longrightarrow 3O_2$, which occurs simultaneously with the reaction $H_2 + O_3 \longrightarrow H_2O + O_2$, with the velocity of deozonisation in the absence of hydrogen. Several determinations of the rate of thermal decomposition of ozone have already been published, the most important being those of Warburg (*Ann. Physik*, 1902, **9**, 1286), Clement (*ibid.*, 1904, **14**, 342), Jahn (*Z. anorg. Chem.*, 1906, **48**, 260), Perman and Greaves (*Proc. Roy. Soc.*, 1908, *A*, **80**, 353), Chapman and Clarke (J., 1908, **93**, 1638), and Chapman and Jones (J., 1910, **97**, 2463). There is general agreement between these authors that the decomposition of ozone, allowed to proceed in clean glass vessels at temperatures up to 150°, is apparently of the second order, a much better bimolecular than unimolecular constant being obtained, and there is also agreement as regards the order of magnitude of the bimolecular velocity coefficient at a common temperature, *e.g.*, 100°. There is conflict of opinion, however, regarding (*a*) the nature of the reaction, whether it is essentially homogeneous or heterogeneous, (*b*) the effect of pressure on the reaction velocity, and (*c*) the effect of addition of inert gases such as nitrogen. Chapman and Clarke believe that the reaction is practically a homogeneous one, while Perman and Greaves consider that their results indicate the surface of the containing vessel to be the main seat of the change. The present work was not undertaken for the purpose of deciding this point experimentally; our attention has been mainly confined to the effect of addition of other gases and variation of the partial pressure of oxygen on the velocity.

Jahn (*loc. cit.*) found that the velocity of deozonisation in mixtures of ozone and oxygen is inversely proportional to the partial pressure of the latter gas, while Perman and Greaves also found an increased velocity on diminishing the pressure of oxygen, although the effect was less than that obtained by Jahn. On the other hand, Chapman and Jones state that variation in the partial pressure of oxygen in ozonised oxygen is unattended by appreciable change in the velocity of deozonisation. The latter investigators were also unable to detect any effect due to admixture with nitrogen, although this was found by Jahn and by Perman and Greaves to increase the rate of decomposition of ozone.

In view of these discrepancies and also as the results would be of interest for comparison with corresponding velocity data for this reaction in the presence of hydrogen, experiments on the rate of deozonisation at 100° in ozonised oxygen at various pressures and in mixtures of ozonised oxygen with helium, with argon, with nitrogen, and with carbon dioxide have been carried out.

Experimental.

The velocity of deozonisation was measured by the static method, the difference in pressure between the reaction tube and a compensator tube, containing air and maintained at the same temperature, being registered by a manometer containing concentrated sulphuric acid.

The apparatus and experimental methods employed were those of Griffith and Shutt and of Griffith and MacWillie (J., 1923, **123**, 2752, 2767) suitably modified; the materials used in this work are also described in the same papers.

All the experiments were carried out at approximately 100°.

The reaction was followed for 2 to 3 hours, after which the reaction and compensator tubes were quickly cooled to room temperature * and the residual ozone was determined analytically. From the amount of ozone thus found, one could calculate the pressure increase which has to be added to the last pressure difference obtained at 100° to give the value of p_∞, the pressure reading which would have been observed had the reaction gone to completion.

If θ_1 = room temperature,* θ_2 = temperature of the steam, p = pressure increase required (expressed in mm. H_2SO_4), v = common volume of reaction and compensator tubes in c.c., z = number of gram-molecules of residual ozone in reaction tube, π_{θ_1} = total pressure at the temperature θ_1 in the reaction tube expressed in mm. H_2SO_4, and γ = volume of the manometer tubing in c.c. per mm., then it may be shown that

$$p = z \times 380 \times 13{\cdot}59 \times 22412 \times (273 + \theta_1) \times R/(1{\cdot}84 \times 273 \times v \times \alpha).$$

Here $\alpha = (1 + \gamma\pi_{\theta_1})/v$ (compare Griffith and Shutt, *loc. cit.*, p. 2756) and R is a factor the value of which would have been equal to the ratio of the absolute temperatures $273 + \theta_2$ and $273 + \theta_1$, had there been no "dead" space at the higher temperature θ_2, and had there been no alteration in the effective volumes of the reaction and compensator tubes owing to the motion of the manometric liquid. The value of R was determined experimentally;

* In reality, the temperature of the town water supply. The value of θ_1 for each experiment is not given in the tables. The mean value for the experiments given in Tables III and IV was 8°.

it depends on the ratio of "dead" space to volume of reaction tube and also on the total pressure; the values found are given in the tables.

Values of the bimolecular velocity coefficients ($k_{obs.}$) were calculated from

$$k_{obs.} = \frac{1}{t_2 - t_1}\left\{\frac{1}{p_\infty - p_2} - \frac{1}{p_\infty - p_1}\right\},$$

p_1 and p_2 being the observed manometric differences at the temperature θ_2 at times t_1 and t_2, respectively (time in minutes).

The coefficients were calculated in all cases between successive time readings, this method being the one best suited to show the magnitude of any "trend" in the constants.

From the values of $k_{obs.}$, the absolute values (k_a) of the coefficients in the units litres/moles-minutes were calculated from the equation

$$k_a = k_{obs.} \times \frac{R}{\alpha} \times (273 + \theta_1) \times 380 \times \frac{13{\cdot}59}{1{\cdot}84} \times 0{\cdot}08207.$$

Four reaction tubes were employed.*

Tube A : of German glass, 42 cm. long and approximately 2 cm. in diameter; volume = 126·5 c.c.; containing 2·0 c.c. of concentrated sulphuric acid spread along its entire length.

Tube B : of German glass, 41 cm. long, 2 cm. in diameter; volume = 125·0 c.c.; containing 3·0 c.c. of concentrated sulphuric acid spread along its entire length.

Tube C : of glass of unknown origin, 31 cm. long, approximately 2·6 cm. in diameter; volume = 153·8 c.c.

Tube D : of English glass, length = 39 cm., diameter = 2·2 cm.; volume = 156·6 c.c.

Most of the experiments were carried out with tube D. Only a few experiments could be carried out with tube A before it cracked, while tube C, though apparently its inner surface was as carefully cleaned as that of the others, gave far higher velocity coefficients and probably contained a trace of some catalytic material. The results of the three experiments performed with this tube are included in the table of results for comparison.

The velocity of deozonisation was determined at 100° with ozonised oxygen under pressures of approximately 330, 540, 760 and 1000 mm. of mercury. Experiments were also carried out at the same temperature, employing mixtures in various proportions of ozonised oxygen with helium, with argon, with nitrogen

* A few preliminary experiments were carried out in a fifth tube. The results (not here presented) agreed well with those obtained with Tubes A, B, and D.

and with carbon dioxide. The total pressure in these cases was either 760 or 1000 mm.

The reaction does not follow a strictly bimolecular course, there being a tendency for the second-order coefficients to increase with time, *i.e.*, with diminishing concentration of ozone. This increase, however, is small in ozonised oxygen mixtures under the highest pressures employed, but becomes rather more marked when the total pressure is reduced. In the presence of excess of any one of the four diluent gases investigated and when the total pressure was 1000 mm. of mercury, no sensible rise in the coefficient with time was observed.

Tables I, II, III, and IV summarise the results. Tables I and II relate to preliminary experiments carried out employing tubes A, B, and C, Tables III and IV to the final series, all the experiments in which were obtained with the same reaction tube D. In these tables, P_{θ_2} = total initial pressure of reaction mixture in mm. of mercury at the temperature θ_2; $p^{0_2}_{\theta_2}$ = sum of initial partial pressures of oxygen and ozone, which may be taken as the mean partial pressure of oxygen during the experiment; and $p^{x}_{\theta_2}$ = partial pressure of the added gas. The values given under $k_{obs.}$ are the highest and lowest values obtained for this bimolecular coefficient; $k^m_{obs.}$ is the weighted mean value of $k_{obs.}$, k^m_a is the absolute value corresponding to $k^m_{obs.}$, and k^m_a (corr.) is this absolute value corrected to a uniform temperature of 100°, using the figure 2·5 obtained by Warburg (*loc. cit.*) for the temperature coefficient of the reaction. The assumption here made, that this temperature coefficient is independent of the total pressure and composition of the gas mixture, can lead to no serious error, since in no case does the temperature of observation deviate from 100° by more than 1·2°.

TABLE I.

Ozone–Oxygen Mixtures.

No. of expt.	Tube.	θ_2.	P_{θ_2}.	α.	R.	$k_{obs.} \times 10^4$.	$k^m_{obs.} \times 10^4$.	k^m_a.	k^m_a (corr.).
5	A	99·5	752	1·123	1·210	1·10—1·37	1·20	8·57	8·98
6	A	99·4	743	1·121	,,	1·15—1·45	1·28	9·14	9·67
7	A	99·7	750	1·123	,,	1·12—1·45	1·27	9·06	9·33
8	A	100·15	754	1·123	,,	1·15—1·45	1·34	9·60	9·47
9	A	99·9	757	1·124	,,	1·15—1·60	1·28	9·13	9·22
10	B	99·9	762	1·124	1·214	1·29—1·64	1·38	9·67	9·76
11	B	99·8	758	1·124	,,	1·20—1·56	1·34	9·39	9·57
13	B	100·2	768	1·125	,,	1·29—1·56	1·41	10·0	9·82
16	B	99·15	743	1·121	,,	1·18—1·47	1·29	9·12	9·88
20	B	100·0	1003	1·162	1·196	1·03—1·45	1·16	7·77	7·77
21	C	100·2	766	1·100	1·246	2·53—5·40	—	—	—
22	C	100·1	763	1·100	,,	2·18—3·86	—	—	—
23	C	100·2	775	1·101	,,	1·84—2·62	—	—	—

Table II.

Mixtures of Ozonised Oxygen with Helium, Argon, and Nitrogen.

No. of expt.	Tube.	Addition.	θ_2.	P_{θ_2}.	$p^{O_2}_{\theta_2}$.	$p^{x}_{\theta_2}$.	α.	R.	$k_{obs.} \times 10^4$.	$k^m_{obs.}$ $\times 10^4$.	k^m_a.	k^m_a (corr.)
14	B	Argon	100·15	768	461	307	1·125	1·214	2·10—2·70	2·25	15·9	15·7
17	B	„	99·4	746	435	311	1·121	„	1·75—2·30	1·99	14·2	15·0
15	B	Nitrogen	99·6	749	414	335	1·121	„	2·06—2·68	2·33	16·5	17·1
18	B	Helium	99·8	755	440	315	1·123	„	1·91—2·48	2·20	15·6	15·8
19	B	„	100·2	767	447	320	1·124	„	2·02—2·81	2·42	17·0	16·7

Table III.

Ozone-Oxygen Mixtures. **Tube D.**

No. of expt.	θ_2.	P_{θ_2}.	α.	R.	$k_{obs.} \times 10^4$.	$k^m_{obs.}$ $\times 10^4$.	k^m_a.	k^m_a (corr.).
41	99·7	335	1·044	1·288	1·84—2·61	1·90	15·1	15·6
47	99·8	335	1·044	„	2·10—2·58	2·15	17·1	17·4
33	100·3	529	1·069	1·269	1·63—2·10	1·70	13·0	12·6
46	99·4	540	1·071	„	1·46—2·03	1·51	11·5	12·2
34	100·0	559	1·073	„	1·68—2·12	1·75	13·4	13·4
24	100·1	766	1·101	1·243	1·34—1·47	1·40	10·2	10·1
25	100·0	755	1·100	„	1·30—1·62	1·37	10·0	10·0
26	99·9	759	1·100	„	1·40—1·63	1·44	10·5	10·6
29	99·8	752	1·099	„	1·42—1·75	1·50	10·9	11·1
36	99·9	753	1·099	„	1·35—1·80	1·40	10·2	10·3
31	100·0	1015	1·133	1·220	1·15—1·38	1·20	8·33	8·33
32	100·2	1021	1·133	„	1·22—1·37	1·23	8·52	8·37

Table IV.

Mixtures of Ozonised Oxygen with Helium, Argon, Nitrogen, and Carbon Dioxide. **Tube D.**

No. of expt.	Addition.	θ_2.	P_{θ_2}.	$p^{O_2}_{\theta_2}$.	$p^{x}_{\theta_2}$.	α.	R.	$k_{obs.} \times 10^4$.	$k^m_{obs.}$ $\times 10^4$.	k^m_a.	k^m_a (corr.).
39	Nitrogen	99·8	1003	334	669	1·133	1·220	3·32—3·68	3·46	24·1	24·6
44	Helium	99·0	976	325	651	1·128	„	2·56—3·35	2·91	20·3	22·3
45	„	99·0	974	325	649	1·128	„	2·72—3·15	2·86	19·9	21·9
49	„	99·8	1005	335	670	1·133	„	2·87—3·18	3·00	20·8	21·2
42	Argon	99·4	993	331	662	1·132	„	3·40—4·46	3·94	27·4	29·0
43	„	99·3	984	328	656	1·130	„	3·48—4·00	3·73	26·0	27·8
48	„	99·9	1012	337	675	1·133	„	3·90—4·40	4·11	28·5	28·8
40	CO_2	99·9	1004	335	669	1·133	„	3·29—3·76	3·48	24·2	24·4
37	Nitrogen	100·2	1016	762	254	1·133	1·220	1·57—1·91	1·65	11·4	11·2
38	Helium	100·3	1026	770	256	1·134	„	1·51—2·27	1·57	10·9	10·6
27	Helium	99·7	751	441	310	1·100	1·243	2·17—2·45	2·30	16·8	17·3
28	Nitrogen	99·7	750	456	294	1·100	„	2·01—2·63	2·15	15·8	16·2
35	CO_2	99·6	754	440	314	1·100	„	2·22—2·53	2·35	17·7	17·7
30	Nitrogen	100·3	766	519	247	1·101	1·243	2·10—2·62	2·20	16·0	15·5

The velocity of deozonisation in ozonised oxygen obtained with tube C (Table I, experiments 21—23) is much higher than that found employing any of the other tubes with the reaction mixture

at the same total pressure of 760 mm.; also the relative increase in the coefficient as the reaction proceeds is greater. Experiments 21—23 were carried out in the order given and it is of interest to note that the catalytic material of unknown nature present on the surface of the tube was gradually being rendered less active, as evidenced by the progressive fall in the velocity coefficients; possibly, had work with this tube been continued, the constant $k_{obs.}$ would eventually have fallen to the value obtaining in the other tubes. In connexion with this change of catalytic activity of the surface of the reaction vessel, a somewhat analogous effect was observed with tube D. After the experiments given in Tables III and IV had been completed, a fresh series carried out in the same tube (D) gave uniformly smaller coefficients than those recorded in Tables III and IV. Table V summarises a few of these experiments. The constants are now of the order of 10% less than those previously obtained under analogous conditions.

TABLE V.

Tube D.

No. of expt.	Addition.	θ_2.	P_{θ_2}.	$p^{\theta_2}_{\theta_2}$.	$p^{x}_{\theta_2}$.	a.	R.	$k_{obs.} \times 10^4$.	$k_{obs.}$ $\times 10^4$.	k^m_a.	k^m_a (corr.).
54	—	98·85	758	758	—	1·100	1·243	1·08—1·28	1·12	8·11	9·04
55	—	100·5	1029	1029	—	1·134	1·220	1·11—1·21	1·16	8·03	7·66
56	—	100·3	335	335	—	1·104	1·288	1·78—2·52	1·98	15·7	15·2
50	Argon	99·35	993	745	248	1·130	1·220	1·52—1·80	1·54	10·7	11·4
51	Nitrogen	99·0	984	738	246	1·129	„	1·24—1·53	1·32	9·16	10·1
52	Helium	99·0	976	734	245	1·129	„	1·21—1·57	1·27	8·85	9·75
58	Argon	99·8	1006	405	601	1·132	1·220	2·96—3·90	3·11	21·6	22·0
57	Helium	100·0	1015	409	606	1·133	„	2·24—2·89	2·44	17·0	17·0

The coefficients obtained with tubes A and B containing sulphuric acid (Tables I and II) are only slightly lower than those obtained under identical conditions of pressure and composition of gas mixture in tube D, which contained no sulphuric acid (Tables III and IV). Since the catalytic effect of the glass surfaces of tubes A and B might have differed from that of D, a few experiments were carried out with tube D to test the effect of addition of sulphuric acid. The velocity coefficient was first determined for ozonised oxygen at a pressure of 755 mm., 3·9 c.c. of concentrated sulphuric acid were introduced into the tube so that it spread over its whole length (approximately one-eighth of the inner surface was covered by the acid), and the velocity coefficient was redetermined with the following results :—

Expts. 59 and 62 : No H_2SO_4 present; k^m_a (corr.) $= \left.\begin{matrix} 9{\cdot}71 \\ 9{\cdot}87 \end{matrix}\right\} 9{\cdot}79.$

Expts. 63 and 64 : In presence of H_2SO_4; k^m_a (corr.) $= \left.\begin{matrix} 9{\cdot}31 \\ 9{\cdot}45 \end{matrix}\right\} 9{\cdot}38.$

A slight diminution in the value of the velocity coefficient is therefore caused when part of the glass surface is replaced by one of sulphuric acid.

Discussion of Results.

Tables III and IV contain the main results of this work and summarise a number of determinations of the velocity of deozonisation at 100° under various conditions. These data were obtained with the same reaction tube D, and with (it is believed) its surface in a constant condition as regards possible catalytic action.

The tables show that :—

(*a*) The velocity of deozonisation in mixtures containing only ozone and oxygen is a function of the oxygen pressure, as already found by Jahn and by Perman and Greaves, but later contradicted by Chapman and Jones. We find that the velocity coefficient increases with decreasing total pressure, but the two quantities are not inversely proportional as stated by Jahn, rather their product diminishes as the pressure decreases. Actually it is found that the variation of k_a^m with pressure in tube D is very closely reproduced by the empirical relation $k_a^m = 11{,}500/(360 + P_{\theta_2})$.

The absolute values of the bimolecular velocity coefficient found by us are in fair agreement with those obtained by Warburg and by Perman and Greaves at the same temperature and under corresponding conditions of pressure. Thus, for ozonised oxygen at 100° and a pressure of 1000 mm. of mercury, we find $k_a^m = 7{\cdot}77$ for tube B and 8·35 for tube D, while Warburg gives a mean value, $k_a^m = 7{\cdot}54$. At 100° and 758 mm. pressure, our value of k_a^m (tube D) = 10·3 agrees fairly closely with that calculated from the results given by Perman and Greaves (Globe II), *viz.*, 9·72.

(*b*) The addition of any one of the gases nitrogen, argon, helium, and carbon dioxide causes an increase in the velocity of deozonisation, if the reaction velocity in the presence of one of these gases is compared with that found in ozonised oxygen alone with the same partial pressure of oxygen. In virtue of (*a*), this increase is still more pronounced if the coefficient found in the presence of one of these gases is compared with that observed in ozonised oxygen under the same *total* pressure. This increase in velocity is very marked when the partial pressure of the added gas is large. Thus the velocity coefficient k_a^m for ozonised oxygen at a pressure of 335 mm. is about 16·5 (mean of the results of experiments 41 and 47), whilst, in a mixture containing oxygen at the same partial pressure, but with a partial pressure of argon of 660 mm., the constant is now 28·5 (experiments 42, 43, and 48).

The increased velocity of deozonisation caused by addition of nitrogen is in qualitative agreement with the results of Jahn at

the higher temperature 127°, and of Perman and Greaves at 100°. Quantitatively, however, the relative increase in the coefficient observed by the latter investigators is somewhat greater than that obtained in the present work with the same gas mixture. On the other hand, Chapman and Jones could not detect any increase in the rate of reaction resulting from displacement of part of the oxygen in ozonised oxygen by nitrogen.

(*c*) The positive catalytic effects of the four gases investigated are in the order argon greatest, followed by nitrogen and carbon dioxide with approximately equal effects, and helium least. This order bears no relation to the catalytic effects found for these gases by Griffith and MacWillie on the rate of photochemical decomposition of ozone by visible light.

A necessary preliminary to any attempt at an explanation of the results presented in this paper appears to involve an answer to the question as to whether the decomposition of ozone under the conditions here investigated occurs mainly in the homogeneous gaseous phase or at the glass surface of the containing vessel. We are unable from the results of the present work or from the results of previous workers to arrive at a definite conclusion on this point. All that may safely be inferred is that some part at least of the measured rate is due to a heterogeneous change. This is shown by the slight variation in the velocity coefficient from tube to tube and by the retarding effect produced by covering a portion of the glass surface by sulphuric acid. We believe that our results may best be interpreted in the following way. The main reaction is a homogeneous change and is accompanied by a heterogeneous reaction whose velocity involves a lower power of the ozone concentration. This would explain the increase in the value of the bimolecular coefficient in each experiment with time, and in particular the relatively greater increase of this function with time the lower the pressure, *i.e.*, the lower the initial concentration of ozone. The few experiments carried out with tube C (21—23, Table I) support this view. Here apparently we are dealing with a case where the catalytic activity of the surface, and therefore the rate of the heterogeneous reaction, is of far greater significance than in the experiments with the other tubes. It will be observed that in these three cases, the greater the velocity of deozonisation, the greater also is the relative increase in the calculated bimolecular coefficient with time. This result is consistent with the conception of a constant intrinsic rate for the homogeneous process, together with a gradually decreasing catalytic activity of the surface which governs the intrinsic rate of the heterogeneous process.

If the observed reaction is a mixture of homogeneous and heterogeneous changes, which of these is it that the inert gases catalyse? Presumably, it is not the rate of heterogeneous change which is affected, and this for two reasons: (1) the velocity coefficient varies less with time in the presence of an inert gas than in its absence, indicating that the homogeneous change is accelerated relative to the heterogeneous change of lower order; (2) not only is the power of adsorption of such gases as argon and helium by glass surfaces small, but it is difficult to see how such adsorption could produce any other than a retarding effect on a heterogeneous change. We must therefore conclude that the catalytic effect of the inert gases investigated takes place in the gaseous phase.

We have thus to explain the retardation of the velocity of the homogeneous reaction by increase of the pressure of oxygen, and its acceleration by introduction of an inert gas. The effect of oxygen has been interpreted by Jahn (*loc. cit.*) in terms of the reaction scheme : $O_3 \rightleftharpoons O_2 + O$; $O + O_3 \longrightarrow 2O_2$, leading to $k_{obs.} \propto [O_3]^2/[O_2]$. This relation, however, is not in agreement with our experimental results; further, it appears improbable that the energy relations of the process of deozonisation are consistent with the formation of oxygen atoms at a temperature of 100°. If this mechanism be discarded, there remain such possibilities as:

(1) $O_3 \rightleftharpoons O_3^*$; $O_3^* + O_3 \longrightarrow 3O_2$,

where O_3^* represents an activated ozone molecule; or

(2) $O_3 \rightleftharpoons O_3^*$; $O_3^* + O_3 \rightleftharpoons$ complex; complex $\longrightarrow 3O_2$.

A qualitative agreement with the results of the present work may be obtained on the basis of this second possibility, if we make the following assumptions :

(*a*) The complex may either revert spontaneously into ozone molecules or decompose into oxygen molecules.

(*b*) Either of these changes may also be brought about by collision of the complex with an indifferent molecule.

Depending upon the type of the colliding molecule, one of these "decomposition by collision" processes will be favoured at the expense of the other. In this sense our results indicate that collisions with oxygen molecules favour the reversal: complex $\longrightarrow 2O_3$, whereas it is the process: complex $\longrightarrow 3O_2$ which is assisted by collision with inert gas molecules in the order argon, nitrogen, carbon dioxide, helium.

In connexion with the above assumptions, some theoretical considerations regarding the mechanism of chemical reactions which have recently been advanced by Christiansen (*Z. physikal. Chem.*, 1924, **113**, 35) and by Born and Franck (*Z. Physik*, 1925, **31**, 411) are of interest. Christiansen considers the first stage in

a bimolecular reaction to be the formation by collision of an active complex. This complex can subsequently decompose spontaneously into resultants, or can suffer deactivation by collision with a third molecule. Accordingly the probability that reaction should take place is determined by a factor of the form $\rho/(\rho + \Sigma\eta C)$, where ρ denotes the probability of spontaneous reaction, C is the concentration of any molecular species present, and the η's are specific coefficients such that $\Sigma\eta C$ gives the probability of deactivation of the complex by collision. Born and Franck have also dealt with deactivation processes occurring in chemical reactions, but from a somewhat different point of view. They conclude that, in order that additive processes of the type $A + B \longrightarrow AB$ may occur, it is necessary that the activated complex (or quasi-molecule) AB* first formed should, during its life period, suffer collision with a third molecule, whose function is to remove the difference in energy between AB* and AB. [On the other hand, they consider that, for substitution processes as $A + B \rightarrow C + D$ to occur, such ternary collisions are unnecessary.] Accordingly, the reaction velocity coefficient of Born and Franck should contain a function of the type $\Sigma\eta_1 C/(\rho_1 + \Sigma\eta_1 C)$, a function which is in a sense complementary to that of Christiansen; ρ_1, however, now defines the intrinsic probability of the reversal $AB^* \longrightarrow A + B$, and the η_1's refer to the change $AB^* \longrightarrow AB$.

The suggestions made by us in the reaction mechanism for the process of deozonisation include all four of the possibilities of change on the part of the complex entertained by Christiansen and Born and Franck. As a result, our final expression for the bimolecular velocity coefficient would contain a complex probability term of the form $(\rho + \Sigma\eta C)/(\rho + \rho_1 + \Sigma\eta C + \Sigma\eta_1 C)$ in which ρ and η refer to the change : complex $\longrightarrow 3O_2$ and ρ_1 and η_1 to the change : complex $\longrightarrow 2O_3$. As already stated, these possibilities afford a qualitative explanation of our results.

While it is not suggested that the mechanism postulated is necessarily the correct one, we believe that an explanation of the "negative" catalytic effect of oxygen and the "positive" effect of the other gases must involve considerations of the nature indicated above.

Summary.

The velocity of the thermal reaction $2O_3 \longrightarrow 3O_2$ has been determined at 100° in glass tubes in the presence and absence of sulphuric acid. The reaction follows approximately a bimolecular course, the velocity coefficients increasing slightly, however, with time. For ozonised oxygen mixtures, at pressures between 300 mm. and 1000 mm., the bimolecular coefficient k (expressed in the

units litres/moles-minutes) is given by $k = 11{,}500/(360 + P)$, where P = the pressure in mm. of gas mixture.

For mixtures of ozonised oxygen with any one of the gases argon, nitrogen, carbon dioxide, and helium, the velocity of deozonisation is greater than that found for ozonised oxygen with the same partial pressure of oxygen. This positive "catalytic" effect, which is greatest for argon and least for helium, increases with increasing partial pressure of added gas.

A short discussion of these results and of a possible mechanism of the reaction process is given.

The authors' thanks are due to Professor W. C. McC. Lewis for the facilities kindly provided for this work.

THE MUSPRATT LABORATORY OF PHYSICAL AND ELECTRO-CHEMISTRY,
THE UNIVERSITY OF LIVERPOOL. [*Received, May 15th*, 1925.]

CCLXXXV.—*The Dissociation Pressures of Hydrated Double Selenates.*

By JOHN FERGUSON.

IN two former papers (J., 1922, **121**, 1407; 1924, **125**, 1307) the author in conjunction with R. M. Caven communicated an account of the dissociation pressures of hydrated double sulphates of the type $M''SO_4,M'_2SO_4,6H_2O$. The present paper contains the results of measurements of the dissociation pressures of hydrated double selenates of the same type.

The apparatus and methods employed have already been described (*loc. cit.*).

Each double selenate was prepared by crystallisation from a solution containing the two simple selenates in equivalent proportions. Selenium was the starting point in the preparation of the simple selenates. It was converted into copper selenate by Dennis and Koller's method (*J. Amer. Chem. Soc.*, 1919, **41**, 949), and this salt was electrolysed in warm saturated solution (Metzner, *Compt. rend.*, 1898, **127**, 54), yielding selenic acid, from which the simple selenates were obtained by neutralisation with the corresponding carbonates or hydroxides. The double selenates were analysed to test their purity.

The double selenates examined yielded dihydrates as the first stage in their dehydration. Induction lag phenomena were hardly so marked as in the case of the sulphates (J., 1924, **125**, 1308).

The pressures observed are equilibrium pressures in systems of the type $M''SeO_4,M'_2SeO_4,6H_2O \rightleftharpoons M''SeO_4,M'_2SeO_4,2H_2O+4H_2O$.

Copper Potassium Selenate.

Temp.	25·1°	32·5°	39·1°	45·1°	50·7°	61·7°	50·0°	42·7°	36·2°
Press.	11·8	21·7	36·4	55·3	79·9	137·2	77·7	48·3	28·7

Copper Rubidium Selenate.

Temp.	24·9°	32·3°	41·1°	49·6°	59·1°	58·3°	74·8°	67·1°	51·9°	34·4°
Press.	8·0	13·5	24·4	42·4	77·9	73·7	192·0	121·0	49·3	16·2

Copper Cæsium Selenate.

Temp.	27·7°	36·0°	42·7°	50·0°	56·2°	59·2°	65·2°	61·2°	51·2°	32·3°
Press.	22·8	37·9	54·7	81·1	110·5	125·9	164·5	139·1	86·6	48·7

Copper Ammonium Selenate.

Temp.	25·0°	30·6°	35·3°	40·0°	50·8°	60·3°	70·4°	57·3°	44·9°	27·7°
Press.	2·8	5·5	7·5	10·6	26·3	48·5	90·8	38·9	16·2	4·1

Copper Thallous Selenate.

Temp.	29·9°	40·0°	48·0°	53·9°	64·1°	59·2°	44·5°	35·1°
Press.	8·9	20·3	36·3	53·6	99·6	75·0	28·7	13·3

Cobalt Potassium Selenate.

Temp.	26·1°	33·0°	42·5°	48·5°	61·2°	68·2°	43·8°	28·4°
Press.	21·4	33·5	58·5	79·9	148·5	199·2	62·4	26·8

Cobalt Ammonium Selenate.

Temp.	27·0°	34·1°	41·5°	56·3°	65·6°	68·4°	71·1°
Press.	3·4	5·9	10·3	29·7	53·1	64·8	75·5

Zinc Potassium Selenate.

Temp.	31·3°	42·6°	48·5°	57·2°	71·3°	59·9°	37·2°
Press.	23·6	50·7	75·4	120·3	218·3	136·2	36·2

Zinc Ammonium Selenate.

Temp.	31·3°	42·6°	48·5°	57·2°	71·3°	59·9°	37·2°
Press.	2·9	6·9	10·1	19·9	46·5	22·8	4·1

Nickel Potassium Selenate.

Temp.	29·9°	40·0°	48·0°	53·9°	64·1°	59·2°	35·1°
Press.	11·9	25·3	44·4	63·9	119·0	88·7	18·3

Nickel Rubidium Selenate.

Temp.	30·2°	38·2°	52·3°	62·0°	75·9°	54·2°	45·0°
Press.	1·5	3·1	9·0	16·0	37·9	9·9	5·3

Nickel Cæsium Selenate.

Temp.	30·2°	38·2°	52·3°	62·0°	75·9°	54·2°	45·0°
Press.	15·8	26·8	59·4	95·9	157·4	64·8	39·8

Nickel Ammonium Selenate.

Temp.	28·3°	37·2°	43·6°	56·0°	63·2°	69·0°	77·0°	35·6°
Press.	1·0	2·0	3·2	8·2	13·9	20·3	32·2	1·7

Nickel Ammonium Chromate.

This salt was prepared by Brigg's method (J., 1903, **83**, 392). It effloresces slowly in air, forming a brown substance which has the composition of the anhydrous salt. The dissociation pressures of a mixture of the hexahydrated salt and this substance were measured.

Temp.	28·2°	34·8°	40·8°	45·3°	50·7°	56·0°	69·0°	76·7°	57·4°	27·7°
Press.	23·8	34·8	49·4	64·4	84·7	111·7	201·7	278·0	118·8	22·8

Clark and Buckner (*J. Amer. Chem. Soc.*, 1922, **44**, 242) and Clark (*Amer. J. Sci.*, 1924, **7**, 1) have carried out a long series of measurements of the stabilities of ammines of inorganic salts, as indicated by the temperatures at which the dissociation pressures of the ammines rise to a definite value (100 or 760 mm.). They have found that the stability *increases* with *diminishing* atomic volume of the positive part of the molecule, *e.g.*, in the series Cs, Rb, K, Na; Cd, Zn, Mn, Cu, Fe, and *increases* with *increasing* volume of the negative part, *e.g.*, in the series Cl, Br, I; MoO_4, CrO_4, SO_4, SeO_4. These results agree also with the work of Ephraim on the metallic ammines (*Ber.*, 1912, **45**, 1322).

In the following table are given the molecular volumes (determined by Tutton) of both double sulphates and selenates, and also the absolute temperatures at which their dissociation pressures attain a definite value (50 mm.).

Univalent metal or group.	Bivalent metal.	Sulphates.		Selenates.	
		T_{50}.	M.V.	T_{50}.	M.V.
Potassium	Copper	320·8°	197·8	316·6°	211·3
	Cobalt	325·9	197·1	312·5	208·6
	Zinc	327·8	196·2	315·2	208·8
	Nickel	336·8	195·3	323·9	206·1
Rubidium	Cadmium	313·5	216·4	—	—
	Manganese	315·2	213·7	—	—
	Copper	326·0	207·7	325·0	221·5
	Cobalt	335·0	206·5	—	—
	Zinc	339·0	205·6	—	—
	Nickel	346·3	204·8	354·0	217·0
Cæsium	Cadmium	315·0	229·3	—	—
	Manganese	319·9	226·4	—	—
	Copper	332·5	220·3	314·1	235·5
	Cobalt	334·0	219·7	—	—
	Zinc	336·8	218·0	—	—
	Nickel	345·0	217·4	322·8	229·2
Ammonium	Cadmium	317·3	217·5	—	—
	Manganese	317·2	215·5	—	—
	Copper	332·0	207·7	333·7	222·2
	Cobalt	336·8	208·0	337·2	218·1
	Zinc	341·4	206·4	345·0	217·7
	Nickel	354·0	205·5	358·0	216·5

In the case of double salts formed by the same univalent metal or group with different bivalent metals, the temperature at which a pressure of 50 mm. is attained increases with decreasing molecular volume. The constitution of these double salts is probably of the type $M'_2[M''(SeO_4)_2]$, since it is known that in solutions of some of them at least, the bivalent metal migrates partially to the anode during electrolysis. Hence it may be said that stability in the sulphate or selenate groups, taken separately, is favoured by diminishing molecular volume of the anion or negative part of the molecule.

However, it must be pointed out that, although the double selenates have always a much greater molecular volume than the corresponding sulphates, the rubidium and ammonium double selenates are more stable than the rubidium and ammonium double sulphates. The potassium and cæsium double selenates are less stable than the corresponding sulphates.

Nickel ammonium chromate cannot be strictly compared with the sulphate and selenate double salts, as it does not form a dihydrate, like the other two. It is, however, the least stable of the three nickel ammonium salts, and has probably a much greater molecular volume (Tutton, *Min. Mag.*, 1912, **16**, 169).

As regards the positive part of the molecule, it is found that, the bivalent metal being the same, the stability increases with increasing molecular volume of the salt, in the order K, Rb, NH_4. The cæsium salts are anomalous, because, although they have as a class the greatest molecular volume, they are intermediate in stability between the potassium and rubidium salts. This rule, however, does not apply to the cæsium double sulphates of copper, cadmium and manganese, which are more stable than the corresponding potassium and rubidium salts. In the case of the two double selenate groups examined (copper and nickel) the cæsium and potassium dissociation pressure–temperature curves intersect, the cæsium salts being the less stable at lower temperatures.

If the cæsium salts are excluded from consideration, it follows that stability in the series of hydrated double sulphates and selenates is favoured by increasing atomic or molecular volume of the kation or positive part of the molecule.

To sum up, while it is obvious that the specific influence of the various atoms and groups enters as a complicating factor, the results tend to show that the stabilities of the hydrated salts are closely connected with the atomic or molecular volumes of the atoms and groups composing their molecules. The stabilities appear to *increase* with *decreasing* molecular volume of the anion, but increase with *increasing* atomic or molecular volume of the kation.

This relation is opposite to that which obtains with the metallic ammines (Clark and Buckner, *loc. cit.*).

Summary.

1. The dissociation pressures of certain double selenates of the type $M'_2SeO_4,M''SeO_4,6H_2O$ in contact with the corresponding dihydrates have been measured over a range of temperature.

2. The stabilities of these salts, and also of the double sulphates, as measured by the absolute temperatures at which their dissociation pressures attain the value of 50 mm., are greatly influenced by the molecular and atomic volumes of the groups and atoms in the molecule.

3. The specific action of the different atoms and groups introduces irregularities, especially noticeable in the case of cæsium double salts, but in general the stabilities of the hydrates increase with increasing volume of the kation and decrease with increasing volume of the anion.

4. These two relationships are the inverse of those obtaining with the metallic ammines.

The author wishes to thank Prof. R. M. Caven of the Royal Technical College for having suggested this research and for his continued interest in it. He also desires to thank the Carnegie Trust for the provision of a scholarship, which enabled the research to be undertaken.

THE ROYAL TECHNICAL COLLEGE,
GLASGOW. [*Received, July 10th,* 1925.]

CCLXXXVI.—*Researches on Chromammines. Part II. Hydroxopentamminochromic Salts and Electrical Conductivities of Chromammines.*

By HERBERT JOSEPH SEYMOUR KING.

A. *Hydroxopentammino-chromic(-cobaltic) Hydroxide.*

IT was shown in Part I (King, J., 1924, **125**, 1329) that the alkaline solutions obtained by treating chloropentamminochromic or aquopentamminochromic chloride with moist silver oxide, which had until then been regarded as solutions of aquopentamminochromic hydroxide, gave hydroxopentamminochromic picrate with excess of picric acid. (That this is not due to instability of the aquopentamminochromic salt has now been shown by preparing the latter from the nitrate.) Hence the solutions were considered

to contain not aquo– but hydroxo–pentamminochromic hydroxide, a view supported by their intense reddish-violet colour, which is characteristic of " purpureo " rather than " roseo " solutions.

Further investigation showed that the aquopentamminochromic salt was obtained with oxalic acid, which thus behaved similarly to mineral acids (Christensen, *J. pr. Chem.*, 1881, **23**, 26).

$2[Cr(NH_3)_5OH](OH)_2+3H_2C_2O_4=[Cr(NH_3)_5H_2O]_2(C_2O_4)_3+4H_2O.$

2 : 4-Dinitrophenol, a much weaker acid than picric acid, gave the aquo-salt with both the chrommamine and the cobaltammine alkaline solutions. Also picric acid gave the aquo-salt with the cobaltammine solution, though 2 : 4-dinitro-α-naphthol-7-sulphonic acid, a much stronger acid, gave the hydroxo-salt (Part I). In view of these anomalous results, the nature of the alkaline solutions has been investigated from the point of view of electrical conductivity. From measurements of the conductivities of their salts, the conductivities of the aquopentamminochromic and hydroxopentamminochromic ions at zero concentration were found to be 174·3 and 73·3 mhos at 0°, giving 489·3 and 283·3 mhos for the limiting conductivities of the hydroxides. The value obtained by extrapolation of the conductivity data for the chromammine alkaline solution was 283·9, completely confirming the view that it contained only hydroxopentamminochromic hydroxide. The data of Lamb and Yngve (*J. Amer. Chem. Soc.*, 1921, **43**, 2352) for the conductivity of " aquopentamminocobaltic hydroxide " at 0° (ignoring the figure for $c = 0{\cdot}0002683$) give on extrapolation ($n = 1{\cdot}30$) the value 296 at infinite dilution, in fair agreement with the value 287 required for hydroxopentamminocobaltic hydroxide.

Aquopentamminochromic picrate was precipitated, on mixing solutions of aquopentamminochromic nitrate and 200% excess of sodium picrate, as aggregates of golden-yellow needles (Found : Cr, 6·0; NH_3, 9·9; N, 22·9; H_2O, 3·3.

$[Cr(NH_3)_5H_2O]\{C_6H_2O_7N_3\}_3,\frac{1}{2}H_2O$

requires Cr, 6·1; NH_3, 10·0; N, 23·1; H_2O, 3·2%). The salt lost all its water and also 43% of its ammonia on heating at 100° for 3 hours, so this is not a suitable method for introducing the picrato-group into the complex.

Aquopentamminochromic oxalate was obtained on mixing solutions of hydroxopentamminochromic hydroxide (Christensen, *loc. cit.*) and oxalic acid (3 mols.), precipitation occurring on shaking and cooling. It was washed with a little water, and with alcohol until free from oxalic acid. The air-dried product consisted of irregular, orange plates (Found : Cr, 16·3; NH_3, 26·4; H_2O of crystallisation, 10·9. $[Cr(NH_3)_5H_2O]_2(C_2O_4)_3,4H_2O$ requires Cr, 16·1; NH_3, 26·4; H_2O of crystallisation, 11·2%). After a week in a vacuum over phosphoric

oxide, the water of crystallisation was completely removed, together with 4% of the ammonia. The salt lost 47% of its ammonia on heating at 100° for 3 hours, but still retained more than half of the co-ordinated water. Thus it was not possible to prepare an oxalato-salt from it by heating.

Aquopentammino-chromic (-cobaltic) 2 : 4-Dinitrophenoxide.—Finely powdered 2 : 4-dinitrophenol (2 mols.) was shaken mechanically for an hour with a solution of hydroxopentammino-chromic (-cobaltic) hydroxide, when the pure aquopentammino-salt was obtained, the excess of hydroxide remaining uncombined. The sparingly soluble product was washed with water, then triturated and washed with methyl alcohol, leaving a bright yellow powder. Ammonia was estimated as for picrates (Morgan and King, J., 1922, **121**, 1723). A. (Found: Cr, 7·4; NH_3, 11·7; N, 21·3; H_2O, 5·2.

$$[Cr(NH_3)_5H_2O]\{C_6H_3O_5N_2\}_3,H_2O$$

requires Cr, 7·2; NH_3, 11·8; N, 21·2; H_2O, 5·0%). 66% of the ammonia was removed in 3 hours at 85°, together with all the water. B. (Found: Co, 7·7; NH_3, 11·0; N, 20·1; H_2O, 9·2. $[Co(NH_3)_5H_2O]\{C_6H_3O_5N_2\}_3,3H_2O$ requires Co, 7·7; NH_3, 11·1; N, 20·1; H_2O, 9·4%). The compound charred at 100°.

Interaction of Hydroxopentamminocobaltic Hydroxide and Picric Acid Solutions.—Using three mols. of picric acid, the pure aquopentamminocobaltic salt was precipitated (Morgan and King, *loc. cit.*) (Found: Co, 7·1; NH_3, 10·1. Calc., Co, 7·0; NH_3, 10·1%). Two mols. of picric acid gave a mixture of the aquo- and hydroxo-salts.

B. *Hydroxopentamminochromic Salts.*

The only salts of this series hitherto described are the dithionate (Jörgensen, *J. pr. Chem.*, 1882, **25**, 419; Dubsky, *ibid.*, 1914, **90**, 99), picrate and dipicrylamide (Part I). The sulphate, nitrate, chloride, bromide, iodide, chromate and oxalate have now been obtained. They are rose-red salts, much more soluble in water than the corresponding cobaltammines (Werner, *Ber.*, 1907, **40**, 4098). They give solutions only very slightly alkaline to litmus and do not liberate ammonia from ammonium salts in the cold. Thus the tendency to form aquo-salts is less pronounced than in the case of hydroxopentamminocobaltic salts. The co-ordinated hydroxyl group cannot be acetylated or carbonated. Unlike the hydroxopentamminocobaltic salts, they smell of ammonia and are unstable even in the dark. They can, however, be kept indefinitely in an ammoniacal atmosphere. The salts most readily obtained pure and in quantity are the sulphate and nitrate.

That these are not basic aquo- but hydroxo-salts is demonstrated as follows.

(*a*) The sulphate and chromate were obtained anhydrous, whilst the nitrate, bromide, and iodide contained less water than is required for an aquo-salt.

(*b*) Hydroxopentamminochromic picrate was obtained from the sulphate by double decomposition.

(*c*) The electrical conductivities at 25° and a dilution of 1024 litres were of the order required (234 to 268 mhos) for salts with two univalent ions outside the complex, by Werner's empirical rule (Werner and Miolati, *Z. physikal. Chem.*, 1894, **14**, 506). The values obtained for the sulphate, nitrate, chloride, and oxalate were 234·0, 260·8, 274·6 and 235·5. (The value 266·2 obtained for hydroxopentamminocobaltic nitrate also agrees with the rule.)

Hydroxopentamminochromic sulphate was obtained by adding the hydroxopentamminochromic hydroxide solution (100 c.c.) from 4 g. of chloropentamminochromic chloride to 2·17 g. of ammonium sulphate in 3 c.c. of water and 16 c.c. of concentrated ammonia solution. When 50 c.c. of ice-cold alcohol had been added drop by drop to the cooled solution, rosettes of large, rose-red needles began to form. On addition of 20 c.c. more alcohol most of the sulphate crystallised (3·5 g.). It was collected, washed with ammoniacal alcohol and ether, and kept in a vacuum in presence of soda-lime and ammonium carbonate (Found: Cr, 21·2; NH_3, 33·8; S, 13·0. $[Cr(NH_3)_5OH]SO_4$ requires Cr, 20·8; NH_3, 34·0; S, 12·8%).

A sample was triturated with acetic anhydride for 20 minutes. The product was dissolved in water and treated with a solution of sodium picrate. Hydroxopentamminochromic picrate (Part I) was precipitated, showing that no acetylation had occurred (Found: Cr, 8·3; NH_3, 12·8; N, 23·3. Calc., Cr, 7·9; NH_3, 13·0; N, 23·5%).

When carbon dioxide was passed into a cooled concentrated solution of the sulphate, 3 to 4 mols. of ammonia were displaced, an insoluble bluish-violet carbonate of variable composition being formed.

Hydroxopentamminochromic nitrate was not readily obtained by adding the hydroxide to ammonium nitrate solution, as a large excess of alcohol and ether was needed for precipitation and the salt then separated as an oil. Five g. of aquopentamminochromic nitrate (Werner and Surber, *Annalen*, 1914, **405**, 220) were dissolved in 30 c.c. of concentrated ammonia, and cooled alcohol (60 c.c.) was added drop by drop to the ice-cold solution until a permanent crystalline precipitate formed (small, irregular, red plates). This was collected immediately and washed with ammoniacal alcohol and ether (Found: Cr, 18·2; NH_3, 29·6; N, 34·3.

$$[Cr(NH_3)_5OH](NO_3)_2,\tfrac{1}{2}H_2O$$

requires Cr, 18·1; NH_3, 29·7; N, 34·1%). Although the salt had

an ammoniacal odour, it lost only 2½% of its ammonia when kept during 10 weeks over phosphoric oxide in a vacuum.

Action of Pyridine on Aquopentamminochromic Nitrate.—A strong solution of the aquo-salt was treated with excess of ice-cold pyridine, the colour changing from orange to dark red. Addition of alcohol gave an orange precipitate, the ammonia content of which (26·1%) indicated that 25% of the aquo- had been hydrolysed to the hydroxo-nitrate.

Aquopentamminochromic halides, prepared by Christensen (*loc. cit.*) from hydroxopentamminochromic hydroxide, were more conveniently obtained in pure condition as follows.

Chloride.—A solution of 7·5 g. of aquopentamminochromic nitrate in 60 c.c. of water was filtered into 160 c.c. of ice-cold strong hydrochloric acid, when partial precipitation of the crystalline salt occurred. Ice-cold alcohol (100 c.c.) was added and the salt was at once collected (3·7 g.) (Found: NH_3, 32·7. Calc., NH_3, 32·6%). The chlorine was completely and immediately precipitated in the cold by silver nitrate, showing that no chloropentamminochromic salt was present.

Bromide.—A solution of 5 g. of aquopentamminochromic nitrate was added to 60 c.c. of ice-cold strong hydrobromic acid, an immediate precipitate of 5 g. of the bromide being formed. This was freed from a trace of purpureo-salt by dissolving in water (50 c.c.) and filtering into 50 c.c. of ice-cold hydrobromic acid. The *iodide* was prepared similarly to the bromide.

Hydroxopentamminochromic chloride was obtained as aggregates of small, very soluble, rose needles (2 g.) on dissolving aquopentamminochromic chloride (3 g.) in 15 c.c. of concentrated ammonia and slowly adding ice-cold alcohol (60 c.c.) until precipitation was complete. The salt lost 18·6% of its ammonia in 3 hours at 100° (Found: Cr, 21·4; NH_3, 35·0; Cl, 28·9. $[Cr(NH_3)_5OH]Cl_2,H_2O$ requires Cr, 21·4; NH_3, 35·0; Cl, 29·2%).

Hydroxopentamminochromic bromide separated as a solid mass of pink needles when aquopentamminochromic bromide was dissolved in ammonia, and a little ice-cold alcohol added (Found: Cr, 16·3; NH_3, 26·1; Br, 49·5; H_2O, 3·0. $[Cr(NH_3)_5OH]Br_2,\frac{1}{2}H_2O$ requires Cr, 16·1; NH_3, 26·4; Br, 49·5; H_2O, 2·8%).

Hydroxopentamminochromic iodide was obtained as bunches of minute, pink needles by dissolving 5 g. of aquopentamminochromic iodide in 30 c.c. of concentrated ammonia and adding slowly 100 c.c. of ice-cold alcohol. It was somewhat less soluble than the other salts (Found: Cr, 12·7; NH_3, 20·6; I, 60·9. $[Cr(NH_3)_5OH]I_2,\frac{1}{2}H_2O$ requires Cr, 12·5; NH_3, 20·4; I, 60·9%). When solid potassium iodide was added to a solution of aquopentamminochromic nitrate

in concentrated ammonia, an addition compound of the hydroxo-iodide with potassium iodide was obtained (pink needles).

Hydroxopentamminochromic chromate was obtained by adding the hydroxide solution (55 c.c.) from 4 g. of chloropentamminochromic chloride to 2·5 g. of ammonium chromate dissolved in ammonia. The intense reddish-brown solution was treated with alcohol until a permanent crystalline precipitate just formed (aggregates of thin, brown plates). This was collected and washed with ammoniacal alcohol and ether (Found : Cr, 38·7; NH_3, 31·3. $[Cr(NH_3)_5OH]CrO_4$ requires Cr, 38·5; NH_3, 31·5%).

No reduction in weight occurred when the salt was kept for a fortnight over phosphoric oxide.

Hydroxopentamminochromic Oxalate.—The hydroxide solution from 5 g. of chloropentamminochromic chloride (100 c.c.) was added to 2·92 g. of ammonium oxalate in 100 c.c. of water, when ammonia was immediately evolved. Ammonia solution (10 c.c.) was added, and a considerable excess of alcohol and ether; the precipitate of large, pink needles was readily soluble in water (Found : Cr, 18·6; NH_3, 30·4. $[Cr(NH_3)_5OH]C_2O_4,2H_2O$ requires Cr, 18·7; NH_3, 30·6%).

Hydroxopentamminocobaltic Nitrate.—The following is a more convenient method than that given by Werner (*loc. cit.*) for preparing the pure monohydrated salt. To a filtered solution of 20 g. of aquopentamminocobaltic nitrate in 100 c.c. of concentrated ammonia, 240 c.c. of boiling alcohol are added and the mixture is cooled quickly to prevent separation of an oil. The precipitate is dissolved in ammonia, and to the ice-cold filtered solution cooled alcohol is added drop by drop until crystallisation begins (yield 7 g.) (Found : Co, 19·4; NH_3, 28·1. Calc., Co, 19·5; NH_3, 28·1%).

C. *Electrical Conductivities of Chromammines and Cobaltammines.*

The λ–$C^{1/3}$ *Graph* (see Porter, *Trans. Faraday Soc.*, 1919, **15**, 122).—The electrical conductivities of a large number of salts of bivalent chromammine and cobaltammine kations give, for the concentration range $v = 32$ to $v = 1024$, a rectilinear λ–$C^{1/3}$ graph. This has been found to be the case for hydroxopentamminochromic nitrate, chloride and hydroxide, hydroxopentamminocobaltic nitrate, chloropentamminochromic chloride and bromide, chloropentamminocobaltic sulphate, bromide, chloride and nitrate, nitropentamminochromic chloride (xantho), nitropentamminocobaltic nitrite and chloride (xantho), dinitrotetramminocobaltic nitrate (flavo) and chloride (croceo). It has therefore been concluded that in normal cases the λ–$C^{1/3}$ graph for such salts over this range should be rectilinear and that deviations are due to such

phenomena as polymerisation in concentrated solution, hydration and hydrolysis. This view was supported by the fact that in several cases where deviation was found at 25° the graph was rectilinear at 0° (*e.g.*, chloropentamminochromic bromide, Table III). Further, in cases where this graph is rectilinear, extrapolation to zero concentration by means of the $1/\lambda$–$(C\lambda)^{n-1}$ graph gives concordant values for the mobility of the complex ion, whilst extrapolation of data for the same ion which give a curved λ–$C^{1/3}$ graph leads to a quite different mobility value. Thus for the bivalent hydroxopentamminochromic ion, extrapolation of the conductivity data for the nitrate and chloride gives mobility values 131·6 and 131·9 at 25°, whilst the oxalate and sulphate data, which deviate from the straight-line rule (probably owing to polymerisation in concentrated solution), lead to mobility values 380·9 and 195·0.

The rectilinear λ–$C^{1/3}$ graph does not appear to be suitable for extrapolation of conductivity data to infinite dilution, since accurate data for concentrations less than $\frac{1}{1000}$ (*e.g.*, for potassium chloride) are lower than those required by the graph. For ammines of chromium and cobalt it leads usually to results 6% higher at 25° than those obtained by the $1/\lambda$–$(C\lambda)^{n-1}$ graph.

In many cases at $v = 2000$, and sometimes at higher concentrations, the conductivities of ammines are *higher* than those required by the rectilinear λ–$C^{1/3}$ graph. Such data have been considered to be influenced by decomposition of the complex ion, and have been ignored in calculating λ_∞. They are bracketed in the tables.

The rule does not appear to apply to salts of tervalent complex kations. The λ–$C^{1/3}$ graphs for hexammino-chromic (-cobaltic) and aquopentammino-chromic (-cobaltic) salts are curved. Nevertheless, extrapolation leads to concordant results from different salts of the same ion.

Conductivity Data.—The usual Kohlrausch method was employed, resistances being measured by a standardised Post Office box. An open cylindrical cell of constant 0·1197 was used for the salts. The conductivity water was obtained by a single distillation of distilled water with a little potassium bisulphate, and its specific conductivity varied between $0{\cdot}66 \times 10^{-6}$ and $1{\cdot}1 \times 10^{-6}$ mho, at 0°. Except in the case of hexammino-salts, the method of successive dilutions was not employed. A fresh solution was prepared for each measurement, and its conductivity was determined forthwith. This was particularly necessary in the case of hydroxo-salts, since their conductivity increased rapidly when they were kept in contact with the electrodes.

TABLE I.

Hydroxopentammino-chromic and -cobaltic Salts.

v is the reciprocal of the concentration in mols. per litre, and λ the molecular conductivity in mhos.

Bracketed data have been ignored in calculating λ_∞.

	$[Cr(NH_3)_5OH]Cl_2$.		$[Cr(NH_3)_5OH](NO_3)_2$.		$[Cr(NH_3)_5OH]SO_4$.	
v.	$\lambda_{0°}$.	$\lambda_{25°}$.	$\lambda_{0°}$.	$\lambda_{25°}$.	$\lambda_{0°}$.	$\lambda_{25°}$.
32	108·8	206·2	106·4	201·5	(59·4)	(117·6)
64	119·0	225·7	115·7	219·4	(69·5)	(132·9)
128	127·5	239·0	124·7	233·6	(82·0)	(158·3)
256	134·9	253·0	132·0	244·3	(94·1)	(181·2)
512	138·8	261·9	138·9	254·2	(108·3)	(208·2)
1024	147·2	274·6	141·4	260·8	(118·9)	(234·0)
2048	—	—	(152·7)	(279·9)	(132·3)	(254·2)

	$[Cr(NH_3)_5OH]C_2O_4$.	$[Co(NH_3)_5OH](NO_3)_2$.	
v.	$\lambda_{25°}$.	$\lambda_{0°}$.	$\lambda_{25°}$.
32	(132·8)	—	196·5
64	(150·4)	—	215·2
128	(169·6)	124·2	229·5
256	(190·0)	132·2	241·5
512	(213·4)	138·4	(253·4)
1024	(235·5)	143·4	(266·2)

TABLE II.

Hydroxopentamminochromic Hydroxide, $[Cr(NH_3)_5OH](OH)_2$.

α = degree of dissociation.

v	22·53	32·85	42·92	65·70	365·8	∞ (extrapolated
$\lambda_{0°}$	237·8	245·5	250·0	254·1	273·7	283·9
α	83·8	86·5	88·1	89·5	96·4	—

The hydroxide solution was prepared by triturating chloropentamminochromic chloride with moist silver oxide (Christensen, *loc. cit.*), filtering, and washing the oxide with a little ice-cold conductivity water. Air was excluded as much as possible during the preparation, and the conductivity was measured in a stoppered flask-shaped cell. The concentration was determined by an ammonia estimation. The hydroxide prepared from aquopentamminochromic chloride gave similar results. A positive water correction was applied (Lamb and Yngve, *loc. cit.*). The water used was practically "equilibrium water," its specific conductivity being $0{\cdot}66 \times 10^{-6}$ mho at 0°.

TABLE III.

Chloropentamminochromic Salts.

	$[Cr(NH_3)_5Cl]Cl_2$.		$[Cr(NH_3)_5Cl]Br_2$.	
v.	$\lambda_{0°}$.	$\lambda_{25°}$.	$\lambda_{0°}$.	$\lambda_{25°}$.
64	123·1	230·3	—	(232·3)
128	131·1	244·5	134·8	(247·7)
256	137·2	255·0	142·1	(261·5)
512	142·3	264·4	146·8	(272·9)
1024	(147·6)	(276·8)	151·2	(280·6)

The conductivity increased rapidly on standing, particularly in the case of the bromide.

TABLE IV.

Aquopentammino-salts.

v	32	64	128	256	512	1024
$\lambda_{0°}$ for $[Cr(NH_3)_5H_2O]Cl_3$	169·5	186·3	203·4	218·4	232·9	(247·8)
$\lambda_{0°}$ for $[Co(NH_3)_5H_2O](NO_3)_3$	163·0	179·0	197·6	212·2	225·9	238·0

TABLE V.

Hexamminochromic Salts.

	$[Cr(NH_3)_6](NO_3)_3$.		$Cr(NH_3)_6Br_3$.		$[Co(NH_3)_6](NO_3)_3$.		$Co(NH_3)_6Br_3$.
v.	$\lambda_{0°}$.	$\lambda_{25°}$.	$\lambda_{25°}$.	v.	$\lambda_{0°}$.	$\lambda_{25°}$.	$\lambda_{25°}$.
32	—	307·5	—	512	236·3	439·9	453·5
64	182·6	340·2	355·5	1024	250·0	465·9	480·5
128	201·6	375·3	391·1	2048	260·5	489·8	—
256	219·7	408·0	423·3	4096	269·9	512·3	—

The conductivities for hexamminochromic nitrate at 25° are considerably higher than those recorded by Werner and Miolati (*loc. cit.*).

Ionic Mobilities.—The conductivity at infinite dilution has been obtained in every case from the $1/\lambda$–$(C\lambda)^{n-1}$ graph (Noyes and Coolidge, *Carnegie Inst. Pub.*, **63**, 50).

Hydroxopentamminochromic ion. The data for the chloride and nitrate (Table I) give mobility 73·0 and 73·5 ($n = 1·56$ and 1·52) at 0° and 131·9 and 131·6 ($n = 1·60$) at 25°. The means of these closely concordant values are adopted in Table VI. The data for hydroxopentamminochromic hydroxide give mobility 73·9 at 0°, in excellent agreement with the figure derived from the salts.

Hydroxopentamminocobaltic ion. The data for the nitrate (Table I) give mobility 76·6 at 0° ($n = 1·50$) and 131·0 at 25° ($n = 1·60$).

Chloropentamminochromic ion. The data in Table III give the ionic mobility as 75·2 and 76·8 (chloride and bromide) at 0° ($n = 1·50$) and as 139·7 (chloride) at 25° ($n = 1·50$). The data of Werner and Miolati (*loc. cit.*) for the chloride at 25° give a slightly lower value (138·4). The lower figure 75·2 at 0° has been adopted, since the bromide results are probably affected by hydration.

Chloropentamminocobaltic ion. The data of Werner and Miolati (*loc. cit.*; *Z. physikal. Chem.*, 1896, **21**, 235) for chloropentamminocobaltic salts at 25° give an ionic mobility 3·5% higher than that of the corresponding chromammine ion, but extrapolation of the more recent results obtained by Harkins, Hall, and Roberts (*J. Amer. Chem. Soc.*, 1916, **38**, 2643) for the chloride gives values 74·8 at 0° and 140·8 at 25° ($n = 1·60$ and 1·82). These are the values adopted in Table VI.

Aquopentammino-chromic and *-cobaltic ions* at 0°. The data of Table IV give mobilities 174·3 ($n = 1·40$) and 161·7 ($n = 1·44$). The latter agrees well with the estimated value of 160 given by Lamb and Yngve (*loc. cit.*).

Hexamminochromic ion. The data of Table V give mobility 180·0 at 0° ($n = 1·46$) and 369·6 and 370·8 (nitrate and bromide) at 25° ($n = 1·42$ and $1·40$).

The diminution in mobility of the complex ion at 0° on replacing one ammonia molecule of the hexammine by water is 5·7 in the chromammine, 5·3 in the cobaltammine series (see Table VI).

The values employed for the mobilities of the anions at 0° and 25° were Cl′, 41·1 and 75·5; Br′, 43·1 and 77·8; NO_3', 40·4 and 70·6; OH′, 105·0 (0°); $\frac{1}{2}SO_4''$, 78·0 (25°); $\frac{1}{2}C_2O_4''$, 72·7 (25°).

The ionic mobilities of the complex kations are collected in Table VI. Those indicated by an asterisk are taken from the table given by Lamb and Yngve (*loc. cit.*). Q = valency of kation.

TABLE VI.

Kation.	$\Lambda_{0°}$.	$\Lambda_{0°}/Q^2$.	$\Lambda_{25°}$.	$\Lambda_{25°}/Q^2$.
1 : 2-$[Co(NH_3)_4(NO_2)_2]^{\cdot}$	18·1*	18·1	36·3*	36·3
1 : 6-$[Co(NH_3)_4(NO_2)_2]^{\cdot}$	17·9*	17·9	36·1*	36·1
$[Cr(NH_3)_5OH]^{\cdot\cdot}$	73·3	18·3	131·8	33·0
$[Co(NH_3)_5OH]^{\cdot\cdot}$	76·6	19·2	131·0	32·8
$[Cr(NH_3)_5Cl]^{\cdot\cdot}$	75·2	18·8	139·7	34·9
$[Co(NH_3)_5Cl]^{\cdot\cdot}$	74·8	18·7	140·8	35·2
$[Cr(NH_3)_6]^{\cdot\cdot\cdot}$	180·0	20·0	370·2	41·1
$[Co(NH_3)_6]^{\cdot\cdot\cdot}$	167·0*	18·6	327·0*	36·3
$[Cr(NH_3)_5H_2O]^{\cdot\cdot\cdot}$	174·3	19·4	—	—
$[Co(NH_3)_5H_2O]^{\cdot\cdot\cdot}$	161·7	18·0	314·0*	34·9

The mobilities of corresponding chromammine and cobaltammine bivalent ions are practically identical.

The marked increase in mobility of the complex ions with increase of valency has no parallel among ordinary metallic kations. If the mobility is divided by the square of the valency, an approximate constant is obtained throughout the table, showing that the mobility is proportional to the square of the ionic charge. The mean values of Λ/Q^2 for univalent, bivalent and tervalent ions are 18·0, 18·8 and 19·0 at 0° and 36·2, 34·0 and 37·4 at 25°. For metallic kations, Λ/Q is approximately constant.

The author is indebted to the Chemical Society for a grant which has partly defrayed the cost of this investigation.

BIRKBECK COLLEGE,
UNIVERSITY OF LONDON.

[*Received, July 7th*, 1925.]

CCLXXXVII.—*Electrometric Studies of the Precipitation of Hydroxides. Part I. Precipitation of Magnesium, Manganous, Ferrous, Cobalt, Nickel, and Thorium Hydroxides by Use of the Hydrogen Electrode.*

By Hubert Thomas Stanley Britton.

No satisfactory system of classifying the metals according to the strengths of their hydroxides has yet been evolved, although it is this property which underlies the general chemical character of the elements and also many analytical separation processes. Measurements of the basic strength by determinations of electromotive force, of heats of formation of oxides and salts, of dissociation pressures of sulphates at different temperatures, and of the hydrolysis of various salts in solution have led to different arrangements. The arrangement in the order of the dissociation constants of the hydroxides as calculated from hydrolysis data is not altogether satisfactory, for in the majority of cases sufficiently accurate measurements cannot be made.

Curiously enough, the order of the precipitation of the hydroxides by the gradual addition of alkali has received no serious attention, except with regard to the separation of the rare-earths. Hildebrand's work (*J. Amer. Chem. Soc.*, 1913, **35**, 847) in this connexion has been repeated and extended by the present author. A definite hydrogen-ion concentration, within narrow limits, has to be attained before the precipitation of any particular hydroxide can take place. This would be expected from a consideration of the "solubility product." An insoluble hydroxide, MOH, attains equilibrium with undissociated molecules and ions in solution, thus:

$$\text{MOH (solid)} \rightleftharpoons \text{MOH (undissociated)} \rightleftharpoons \text{M}^{\cdot} + \text{OH}'.$$

The "solubility product" $= [\text{M}^{\cdot}][\text{OH}'] = [\text{M}^{\cdot}]K_w/[\text{H}^{\cdot}]$, where $K_w = [\text{H}^{\cdot}][\text{OH}']$. The precipitation of the hydroxide thus depends on the concentration of both the metal- and the hydrogen-ions. In ordinary analytical operations, the concentrations of the metal ions do not vary to any considerable extent and consequently precipitation depends largely on the hydrion concentration. The hydrion concentrations necessary for the precipitation of a large number of hydroxides, which have now been determined, constitute a suitable basis for the classification of the hydroxides. The order is "parallel" to the increasing magnitude of the solubility products, but whether it is that of the basic strengths cannot be stated with certainty; this can be so only if the concentration of undissociated

molecules is the same for each hydroxide—a point about which nothing is known.

The Hydrogen Electrode.

For titrations involving the separation of precipitates, the Hildebrand form of hydrogen electrode was found to be the most convenient; the hydrogen, obtained from a supply under pressure (*e.g.*, a cylinder), could be passed through the solutions at such a rate that thorough mixing could be ensured, and its rapid passage through the electrode tended to free the platinum black from gases such as carbon dioxide and ammonia which were apt to be occluded, and also completely removed any dissolved oxygen from the solutions. The titrations were carried out in the manner already described (J., 1924, **125**, 1576). The uncertain behaviour of the hydrogen electrode (see *loc. cit.*) is no doubt responsible for many of the conflicting statements in the literature, especially with reference to its use in alkaline solutions. Thus Johnson (*Trans. Amer. Electrochem. Soc.*, 1902, **1**, 187) found the electrode to be sluggish, and Allmand (J., 1909, **95**, 2151) concluded that it was untrustworthy in alkaline solutions. Everything depends, however, on the electrode, its method of preparation and its use, for some electrodes are as satisfactory in alkaline as in acid solutions. Efficient electrodes tend to improve with continuous use, and in a few cases electrodes have remained good over a period of three months.

In precipitation reactions the efficiency of the electrode sometimes depends on the nature of the precipitate; the finer the precipitate the less likely is the electrode to give satisfactory results. In general, precipitates merely render the electrode sluggish. No electrode functions in the presence of precipitated sulphur, but this may be due, not to the fineness of the precipitate, but to interaction between the hydrogen and the sulphur.

The hydrogen electrode has some limitations, but these are not so extensive as is generally stated. It can be used in presence of reducible substances such as nitrates and chromates (compare Britton, *loc. cit.*) if the solution is dilute. No electrode gave complete satisfaction in presence of sulphites; in some titrations, however, the initial readings appeared to be approximately true.

The hydrogen electrode is, of course, inapplicable in solutions containing metals more noble than hydrogen. Moreover, Denham and Allmand (J., 1908, **93**, 424) and Denham (*ibid.*, p. 833) found that the hydrogen electrode behaves anomalously in solutions of lead, cadmium, and univalent thallium salts, owing to catalytic reduction of the kations to a state of lower valency. These observations have been confirmed by the author. It was, however,

thought just possible that by having a suitable layer of platinum black, electrodes might be prepared which would not react with these kations; but numerous attempts to do so were fruitless. In view of the fact that the hydrogen electrode is affected by lead ions in solution, it is remarkable that the lead which is usually deposited with the platinum black does not render the electrode useless; in fact, its presence in the latter seems to increase its efficiency as far as titration work is concerned. Denham and Allmand proved conclusively that lead in the electrode is absolutely without any deleterious effect, for they deposited electrolytically a layer of lead on a hydrogen electrode and found that the electrode still gave correct results.

Previous Investigations with the Hydrogen Electrode in Inorganic Chemistry.

The only observations relating to reactions similar to those now described appear to have been made by Bjerrum (*Z. physikal. Chem.*, 1907, **59**, 336; 1910, **73**, 724), Sand and Grammling (*ibid.*, 1908, **62**, 1), Hildebrand and Harned (Orig. Com., 8th Internat. Cong. Appl. Chem., 1912, **1**, 217), Hildebrand (*J. Amer. Chem. Soc.*, 1913, **35**, 847), Blum (*ibid.*, p. 1499; 1916, **38**, 1282), and Hildebrand and Bowers (*ibid.*, 1916, **38**, 785).

Denham (J., 1908, **93**, 41; *Z. anorg. Chem.*, 1908, **57**, 388) employed the electrode extensively for the determination of the hydrolysis of salts. Steady *E.M.F.*'s were obtained in some cases; in others, they oscillated haphazardly from day to day, showing in the case of *M*/64-thorium sulphate solution that the degree of hydrolysis, calculated to the second step [*i.e.*, to $Th(OH)_2SO_4$] varied from 23 to 59%. The author has not observed any such changes with *M*/100-solutions of either the sulphate, chloride or nitrate at 15°, even after the solutions had been kept in stoppered bottles for several weeks. The following data show that the three salts are almost equally hydrolysed, the extent being half the lowest value obtained by Denham for *M*/64-thorium sulphate solution.

Salt.	*E.M.F.* of H_2 electrode against normal calomel.	Percentage hydrolysis calc. to $Th(OH)_4$.
Nitrate	0·434	5·70
Chloride	0·435	5·47
Sulphate	0·437	5·04

Electrometric Titrations with the Hydrogen Electrode.

(1) *Effect of Concentration, Anion, and Precipitant on the Hydrogen-ion Concentrations required for the Precipitation of Hydroxides.*—Experiments were carried out to see what was the effect of change

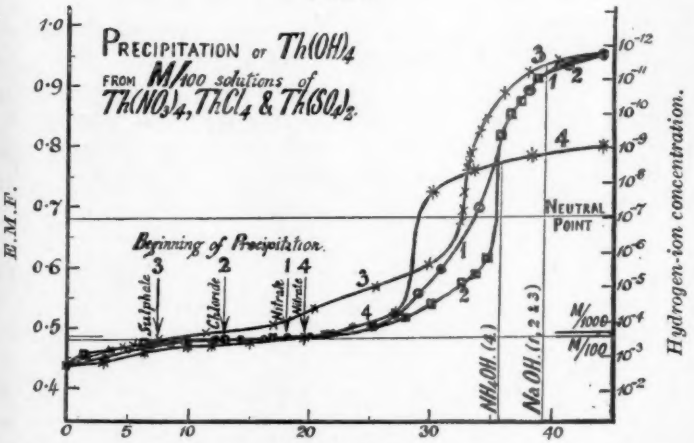
in concentration of salt. The following table gives the p_H values at which thorium hydroxide began to be precipitated by $N/10$-sodium hydroxide at 15° from solutions of thorium nitrate ranging in concentration from $M/1000$ to $M/100$.

Concentration.	*E.M.F.* of H_2 electrode against normal calomel.	p_H.
0·001*M*	0·489	3·60
0·002*M*	0·488	3·58
0·01*M*	0·487	3·57

The difference in p_H is thus very small and this range of concentrations covers those usually employed in analytical work.

Hildebrand found that the p_H's required for the precipitation of neodymia and praseodymia from nitrate solutions were widely

FIG. 1.



(0·1016 *N*-NaOH, *curves* 1, 2 *and* 3. 0·1115 *N*-NH_4OH, *curve* 4).

different from those required in the case of chloride solutions, and he attributed this difference to the nature of the anion (see Part III). The effect of the anion and of the nature of the precipitant has been studied more fully in the case of thorium salt solutions, and again precipitation commenced at the same p_H in all cases (Fig. 1). Curves 1, 2, and 3 represent the titrations of 100 c.c. of $M/100$-solutions of thorium nitrate, chloride, and sulphate respectively, with 0·1016*N*-sodium hydroxide, and curve 4 that of 100 c.c. of $M/100$-thorium nitrate with 0·1115*N*-ammonium hydroxide, at 15°. The commencement of precipitation, *i.e.*, the first appearance of turbidity, is shown by arrows. As a rule, the *E.M.F.*'s were steady (in some cases an hour elapsed before the next reading was taken),

but they were not always so in those stages of the titration which indicated the rapid changes in hydrion concentration occurring at the end of the precipitation. The last section of curve 1 represents a gradual diminution in hydrion concentration and the readings were stationary during the intervals (5 to 15 minutes) allowed for the attainment of equilibrium. Curve 2, chloride, shows a sudden yet well-defined change, but in the case of the thorium sulphate titration (curve 3) the change was irregular and long periods were necessary before constant readings were obtained. Appreciable amounts of alkali had to be added before the commencement of precipitation, and thereafter, in the case of the nitrate and the chloride solutions, there was a distinct tendency for a constant p_H to be maintained during the addition of the greater portion of the alkali. It is probable that this corresponds to the separation of a precipitate of uniform composition.

In neither case was thorium hydroxide precipitated as such. Fig. 1 shows that precipitation was complete and the mother-liquors had become alkaline some time before the stoicheiometrical quantities of alkali had been added. The following table gives the amounts of alkali which were added before precipitation ensued and the amounts of alkali which had to be added before the solutions became neutral (p_H 7).

Curve.	Solution and precipitant.	Precipitation began: p_H.	Precipitation began: Equivs. of alkali.	Equivs. of alkali required for neutrality.
1	$Th(NO_3)_4$ and NaOH	3·57	1·85	3·43
2	$ThCl_4$ and NaOH	3·51	1·30	3·58
3	$Th(SO_4)_2$ and NaOH	3·53	0·78	3·31
4	$Th(NO_3)_4$ and NH_4OH	3·57	2·21	3·24

The last column of the above table shows that the precipitate formed in each titration was basic, being somewhat less so when the precipitant was ammonia. Thus the amount of precipitant required to render the solution neutral in titration No. 4 indicates that the composition of the precipitate was $Th(OH)_{3·24}(NO_3)_{0·76}$, whereas in No. 1, where sodium hydroxide was used, it was $Th(OH)_{3·43}(NO_3)_{0·57}$. The protracted inflexions produced during the last stages of precipitation show that the precipitates at first formed were less basic and suffered some decomposition on further addition of alkali. This seems to have taken place readily in the cases of the nitrate and the chloride, but the slowness with which apparent equilibrium was attained in the second part of the sulphate titration indicates that the basic sulphate was undergoing hydrolysis with much greater difficulty. It seems almost unnecessary to say that the amounts of acid radical retained by these precipitates

were too great to be accounted for by adsorption from such dilute solutions. These precipitates were not completely decomposed even when excess of alkali was added.

Halla (*Z. anorg. Chem.*, 1912, **79**, 260) made a similar observation with thorium nitrate solutions. He found that at room temperature the solution became alkaline to phenolphthalein on the addition of 3·54 equivalents of potassium hydroxide, and on boiling, with 3·60 equivalents.

Another remarkable fact arising from these titrations is that alkali ranging in amounts from 0·78 to 2·21 equivalents to one molecule of thorium salt had to be added before the appearance of a precipitate. These amounts, which vary with the nature of the anion and the precipitant, do not permit of a guess as to the way in which the thorium hydroxide, or basic complex, is held in solution until the attainment of the p_H requisite for precipitation. According to Ordway (*Amer. J. Sci.*, 1858, **26**, 197), Berzelius observed that when alkali was added to a thorium sulphate solution precipitation was delayed owing to the formation of what appeared to be *un soussel soluble*. Ordway directed attention to several other examples of "soluble basic salt" formation. It will be shown in the course of this series of papers that these so-called soluble basic salts exert a pronounced influence on some of the reactions of the metals of which they are characteristic. It is surprising that "soluble basic salts" are generally formed by those metals the valencies of which are greater than two, although this is the case neither with the tervalent rare-earths nor with bivalent beryllium, which has a remarkable property of forming these basic solutions.

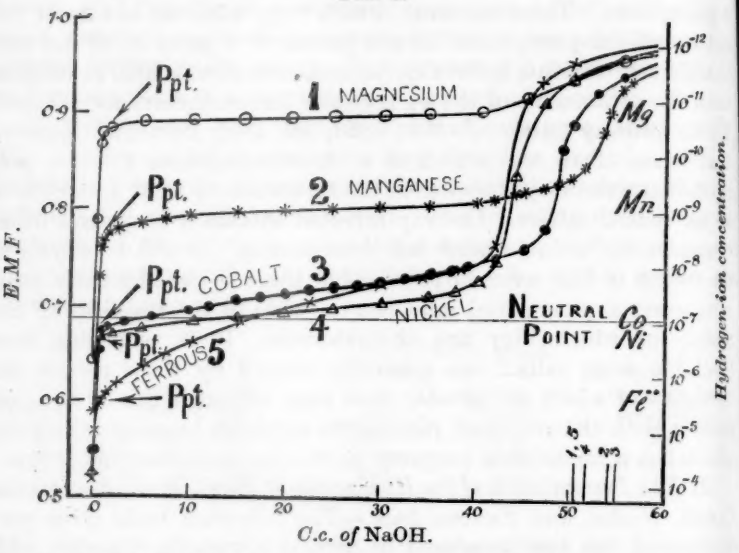
(2) *The Precipitation of the Hydroxides of Magnesium, Manganese, Cobalt, Nickel, and Ferrous Iron.*—The following table gives particulars of the solutions used in typical titrations, together with the amount of alkali required to cause incipient precipitation. The courses of the titrations are shown in Fig. 2.

Titration and curve No.	Temp.	Solution titrated. 100 C.c.	Normality of NaOH.	C.c. of NaOH theoretically required.	Precipitation first began		
					E.M.F.	p_H.	C.c. of NaOH.
1	16°	0·025*M*-$MgSO_4$	0·0990	50·5	0·885	10·49	1·6
2	18	0·024*M*-$MnCl_2$	0·0900	54·0	0·770	8·41	1·0
3	18	0·0247*M*-$CoCl_2$	0·0900	54·8	0·676	6·81	0·9
4	17	0·025*M*-$NiCl_2$	0·0967	51·7	0·666	6·66	0·6
5	17	0·025*M*-$FeSO_4$	0·0990	50·5	0·599	5·49	0·8

In contrast with the thorium salt titrations, the first few drops of sodium hydroxide caused a rapid diminution in hydrion concentration until a value was obtained at which precipitation commenced. Thereafter, precipitation proceeded with very little change

in p_H until the separation was nearly complete. The titration of ferrous sulphate solutions was a matter of some difficulty. As is well known, manganous and ferrous hydroxides on exposure to air readily become oxidised, and consequently the titrations involving their precipitation were performed in vessels which were stoppered as far as possible. Even so, it was not possible to prevent some oxidation from taking place, although plenty of hydrogen was passing through the solutions. The curves, however, were reproducible and there is little doubt that the voltage readings indicated correctly the changes in hydrion concentration. Further support

FIG. 2.



for the belief that the electrodes were behaving normally may be found in the following observations. Atkins (*Trans. Faraday Soc.*, 1923, **18**, 310) found colorimetrically that the precipitation of manganous hydroxide from manganous chloride solutions took place between p_H 8·6 and 9·2 and of ferrous hydroxide from ferrous sulphate solutions between p_H 5·1 and 7·6. Patten and Mains (*J. Assoc. Off. Agric. Chem.*, 1920, **4**, 233) gave p_H 5·5 to 6·0 for ferrous hydroxide.

Precipitation was again complete in each case some time before the theoretical amount of alkali had been added. Curve No. 1, magnesium sulphate, shows that the final inflexion began when 1·64 equivalents of sodium hydroxide had been added The gradual slope of the inflexion was evidently due to the partial decomposition of the basic sulphate, originally precipitated. A similar inflexion,

but steeper, took place in magnesium chloride titrations. Hildebrand and Harned (*loc. cit.*) and Hildebrand (*loc. cit.*) have also studied by means of the hydrogen electrode the precipitation of magnesium hydroxide and have suggested that the electrometric titration of hydrochloric acid solutions of dolomite might be used for the estimation of the magnesia with an accuracy of about 1%, despite the fact that the values obtained by them showed a variation of 5%. The difficulty is that magnesium hydroxide is not precipitated simply from either chloride or sulphate solutions to give sharp inflexions, but indefinite basic precipitates are formed which give poorly defined inflexions; this renders it impossible to assign a point on the curve which exactly corresponds to the neutralisation of all the acid which was originally combined with the magnesium hydroxide. According to Kolthoff (*Rec. trav. chim.*, 1922, **41**, 787), Pinkof (Thesis, Amsterdam, 1919, p. 34) has investigated the electrometric estimation of magnesia by means of the Hg|HgO|Alkali electrode, but obtained unsatisfactory inflexions, even when an excess of alkali was added and the free alkali afterwards titrated. Kolthoff recommended shaking the magnesium salt solution with an excess of alkali and allowing to stand so as to render the decomposition of the basic salt as complete as possible before titration.

Precipitation was complete from (*a*) manganous chloride solution —curve 2—on the addition of about 1·93 equivalents of sodium hydroxide, (*b*) cobalt chloride solution—curve 3—1·75 equivalents, (*c*) nickel chloride solution—curve 4—1·66 equivalents, and (*d*) ferrous sulphate solution—curve 5—1·71 equivalents. Pickering (J., 1907, **91**, 1981) observed that complete precipitation had taken place from ferrous sulphate solutions at the point where they became alkaline to phenolphthalein, and this was when sodium hydroxide had been added in amounts which varied from 1·77 to 1·86 equivalents. He considered this sufficient justification for the assertion that the precipitate was a definite basic salt, $10FeO,SO_3$. In the present titration the alkali required was somewhat less, probably owing to the slowness with which it was added (a period of 2 hours), which caused the precipitation of a sulphate less basic than Pickering's.

Although basic precipitates were always produced, it is possible to calculate from the curves the values of the solubility products of the hydroxides, which are in good agreement with those obtained by other methods. As a rule, precipitation began somewhere near the point of the first inflexion, although often at a p_H which was a little less than that at which the main precipitation took place. This was probably due to the precipitate having been formed at a point in the solution where the precipitation value of p_H had been temporarily exceeded, and time not having been allowed for its

re-solution. If, therefore, the two straight portions of the curve be produced, it is probable that the point of intersection corresponds more nearly to the amount of alkali which had to be added to produce incipient precipitation, and also to the actual hydrion concentration at which precipitation under ideal conditions would commence. This point represents the limiting conditions necessary to form a precipitate. The concentration of metal ions can be calculated from the amount of alkali, and K_w at 18° being $0{\cdot}73 \times 10^{-14}$, the concentration of hydroxyl ions can be found. Columns 2 and 5 in the following table give the co-ordinates of these points for the curves shown in Fig. 2.

No.	*E.M.F.*	p_H.	p_{OH}.	C.c. of NaOH.	$C_{M^{\cdot\cdot}} \times 10^4$.	$[Me^{\cdot\cdot}][OH']^2$.
1	0·892	10·61	3·52	0·5	2·5	$2{\cdot}3 \times 10^{-11} = [Mg^{\cdot\cdot}][OH']^2$
2	0·794	8·85	5·27	1·0	4·5	$1{\cdot}3 \times 10^{-14} = [Mn^{\cdot\cdot}][OH']^2$
3	0·680	6·92	7·22	1·0	4·5	$1{\cdot}6 \times 10^{-18} = [Co^{\cdot\cdot}][OH']^2$
4	0·675	6·81	7·32	0·8	3·9	$8{\cdot}7 \times 10^{-19} = [Ni^{\cdot\cdot}][OH']^2$
5	0·615	5·77	8·37	0·6	3·0	$4{\cdot}5 \times 10^{-21} = [Fe^{\cdot\cdot}][OH']^2$

The method is, of course, open to the objections (*a*) the difficulty of estimating accurately the amount of alkali required, and (*b*) the fact that basic salts were actually precipitated which may have had some effect on both the hydroxyl- and the metal-ion concentrations.

As a result of their conductivity determinations at 18°, Kohlrausch and Rose (*Z. physikal. Chem.*, 1893, **12**, 241) obtained a value of $3{\cdot}4 \times 10^{-11}$ for the solubility product of magnesium hydroxide. Calculation from the solubility data of Lovén (*Z. anorg. Chem.*, 1896, **11**, 404) gives values ranging from 2·7 to $9{\cdot}2 \times 10^{-11}$. These values are of the same order as the one obtained in this work.

Sackur and Fritzmann (*Z. Elektrochem.*, 1909, **15**, 845) carried out a conductimetric titration of manganous sulphate with barium hydroxide and obtained the value 4×10^{-14} for $[Mn^{\cdot\cdot}][OH']^2$, in agreement with the value $1{\cdot}3 \times 10^{-14}$, given in the table.

No values appear to have been found for the hydroxides of cobalt and nickel. Those reported for ferrous hydroxide are very discrepant; Müller (*Z. Elektrochem.*, 1908, **14**, 77) records $1{\cdot}64 \times 10^{-14}$ at 18°, and Krassa (*ibid.*, 1909, **15**, 491) $8{\cdot}7 \times 10^{-14}$. On the other hand, Müller ("Das Eisen und seine Verbindungen," 1917, pp. 180, 199) calculated, from Bodländer's formula (*Z. physikal. Chem.*, 1898, **27**, 66), which involves the heat of formation of ferrous hydroxide and the decomposition potentials of the two ions, the value $2{\cdot}51 \times 10^{-21}$, which is in remarkable agreement with the value $4{\cdot}5 \times 10^{-21}$ given by titration. The observations of Hildebrand (*J. Amer. Chem. Soc.*, 1913, **35**, 847) on the titration of

ferrous sulphate are in no way similar to the present ones, for the precipitation of ferrous hydroxide did not commence until a considerable proportion of alkali had been added.

These curves throw considerable light on the function of ammonium salts in preventing the precipitation of certain hydroxides. The addition of ammonium salts to ammonia may be such that the p_H is depressed below the precipitation value of either magnesium or manganous hydroxide. The approximate hydrogen-ion concentration of a solution containing ammonium hydroxide and ammonium chloride is given by

$$[H^{\cdot}] = \frac{[NH_4Cl]K_w}{[NH_4OH]K_{NH_4OH}},$$

where $K_w = 10^{-14\cdot14}$ and $K_{NH_4OH} = 10^{-4\cdot64}$ at 18°.

If ammonium chloride is regarded as being completely dissociated, the minimum number of molecules of ammonium chloride to be added to each molecule of ammonia to increase the hydrion concentration to that required just to start precipitation of (*a*) magnesium hydroxide is 0·08, (*b*) manganous hydroxide, 4·5, (*c*) cobaltous hydroxide, 380, and (*d*) hydroxides of nickel and ferrous iron, still more. In analytical processes, the condition for the prevention of the precipitation of the hydroxides of magnesium and manganese is easily satisfied, but the sole cause of the partial or non-precipitation of the other hydroxides is the magnitude of the quantities of ammonium chloride that must be added. Herz (*Z. anorg. Chem.*, 1900, **23**, 227) believed that the behaviour of ammonium chloride in depressing the hydroxyl-ion concentration was also the cause of the non-precipitation of zinc hydroxide, but, as will be shown in the next paper, zinc hydroxide is precipitated while the mother-liquor is still very slightly acid and consequently its precipitation could not be affected by the ammonium salt in the same way as in the foregoing instances. It is more probable, as has been suggested by several investigators, that it is the ammonia itself which maintains the hydroxides of zinc, cobalt, and nickel in solution through the formation of complex ions. No explanation, however, appears to be forthcoming to account for the small effect which ammonium chloride has on the precipitation of ferrous hydroxide. The researches of Lovén (*loc. cit.*), Treadwell (*Z. anorg. Chem.*, 1903, **37**, 326), and Herz and Muhs (*ibid.*, 1904, **38**, 138) have all led to the conclusion, given more directly by these titrations, regarding the influence of ammonium salts in preventing the precipitation of magnesium hydroxide. There are no grounds for attributing it to the formation of a complex magnesium anion—an explanation which is still to be found in some text-books.

Summary.

(1) The reactions between sodium hydroxide and solutions of magnesium, bivalent manganese and iron, cobalt, nickel and thorium salts have been studied by means of the hydrogen electrode.

(2) In every case, the precipitate of hydroxide contained an appreciable proportion of unattacked acid radical.

(3) Hydrogen-ion concentrations, which are peculiar to the various hydroxides, are independent of both the anion and the precipitant, and are only slightly influenced in dilute solutions by changes in concentration of the metallic salts, have to be attained before any particular hydroxide can be precipitated.

(4) The dependence of these hydrion concentrations on the solubility products of the different hydroxides has been shown by calculation, from the respective titration curves, of solubility products which are in agreement with values obtained by other methods.

(5) The well-known effect of ammonium salts in preventing the precipitation by ammonium hydroxide of magnesium and manganous hydroxides has been shown, more directly than has been the case hitherto, to be due to the incapacity of ammonia to produce hydrogen-ion concentrations which are less than those necessary for the precipitation of the respective hydroxides, provided that the ratio of ammonium salt to ammonia be sufficiently large.

The author takes this opportunity to acknowledge his indebtedness to the Department of Scientific and Industrial Research for a personal grant, and to Prof. J. C. Philip, F.R.S., for kindly placing facilities at his disposal.

Imperial College of Science and Technology,
South Kensington. [*Received, June 9th*, 1925.]

CCLXXXVIII.—*Electrometric Studies of the Precipitation of Hydroxides. Part II. The Precipitation of the Hydroxides of Zinc, Chromium, Beryllium, Aluminium, Bivalent Tin and Zirconium by Use of the Hydrogen Electrode, and their Alleged Amphoteric Nature.*

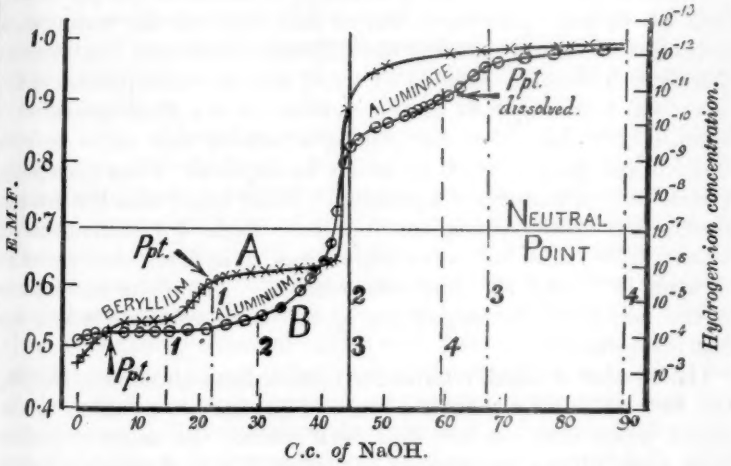
By Hubert Thomas Stanley Britton.

In this part of the work, those hydroxides, including zirconium hydroxide, which are generally supposed to have both basic and acidic properties have been studied, first with respect to their

precipitation, and secondly with respect to the changes in hydrion concentration produced when they react with sodium hydroxide in various proportions. It is very doubtful whether zirconium hydroxide is amphoteric; Hildebrand (*J. Amer. Chem. Soc.*, 1913, **35**, 847), however, has obtained electrometric evidence for the existence of zirconates.

Aluminium and Beryllium Hydroxides.—Hildebrand (*loc. cit.*) and Blum (*ibid.*, p. 1499) observed that on titrating aluminium salt solutions with sodium hydroxide, using the hydrogen electrode, a characteristic inflexion was produced in the curve which corresponded to the formation of sodium monoaluminate. It was

FIG. 1.



therefore decided to see if inflexions were also given in the titration curves of the other so-called amphoteric hydroxides.

The following two solutions (100 c.c.) were titrated at 17°, and the *E.M.F.*'s of the hydrogen electrode compared with that of the normal calomel electrode, saturated potassium chloride solution being the junction liquid. The curves are given in Fig. 1.

Soln. titrated.	Normality of NaOH.	C.c. of NaOH theoretically required.	Precipitate first appeared. *E.M.F.*	p_H.	C.c. of NaOH.
0·00667*M*-$Al_2(SO_4)_3$	0·090	44·4	0·521	4·14	5·0
0·02*M*-$BeSO_4$	0·090	44·4	0·610	5·69	23·0

Neither Hildebrand nor Blum directed attention to the fact that precipitation was complete before the theoretical amount of alkali had been added. The present titration (Fig. 1) shows that precipitation did not begin until 5 c.c. of alkali had been added,

when the dissolved aluminium sulphate had attained the composition given by the formula $Al_2O_3,2{\cdot}65SO_3$, and was complete when 42·2 c.c. (= 5·7 equivalents to 1 mol. of Al_2O_3) of alkali had been added, thereby showing that the basic precipitate contained $Al_2O_3,0{\cdot}15SO_3$. Williamson (*J. Physical Chem.*, 1923, **27**, 284) found that the precipitates formed by the addition of 2 to 4 equivalents of sodium hydroxide were of nearly constant composition and approximated to $Al_2O_3,0{\cdot}6SO_3,3H_2O$. Miller (*U.S. Public Health Reports*, 1923, **38**, 1995) investigated the precipitation from aluminium sulphate solutions by means of alkali and measured the variation in the p_H of the mother-liquors colorimetrically. For additions of sodium hydroxide up to 5 equivalents, the precipitates were similar in composition to those of Williamson, the p_H varying from 4·0 to 5·5. The curve shows that this was the variation in hydrion concentration during the addition of the first 5 equivalents of sodium hydroxide (= 37·0 c.c.) and save for that portion of the curve which corresponds to the addition of the fifth equivalent—between 29·6 and 37·0 c.c.—the gradient of the curve is both uniform and gradual such as would be expected if the precipitate formed were of uniform composition. Miller found that the greatest insolubility of the precipitate occurred when 5·5 equivalents of sodium hydroxide had been added and a hydrion concentration between $10^{-6{\cdot}7}$ and 10^{-7} had been reached. This state corresponds to the maximum decomposition of the basic sulphate which was first precipitated.

The amount of alkali required to form sodium aluminate, $NaAlO_2$, was 59·2 c.c., and although a trace of precipitate remained undissolved when that amount had been added, the solution became quite clear on the addition of a further 2 c.c. of alkali. During the process of re-solution of the aluminium hydroxide, there was a marked depression in the hydroxyl-ion concentration as shown by the inflexion of the curve which was similar to that previously observed by Hildebrand and by Blum. This inflexion seems to provide definite evidence for the existence of an aluminate in solution. As will be shown, in no other instance of the so-called amphoteric hydroxides is such an inflexion produced. Incidentally, in all cases the amounts of alkali required to dissolve the hydroxides, except that of zirconium, which does not dissolve, are considerably in excess of that denoted by the formulæ of the salts which have been said to be formed. In the case of aluminium hydroxide only is the amount of alkali required for its re-solution approximately equal to that suggested by the formula, $NaAlO_2$, and is also independent of the concentration of the sodium hydroxide used (compare Britton, *Analyst*, 1921, **46**, 363). It is possible that the other

hydroxides may be acidic in their behaviour towards alkalis, but to so small an extent that the hydrogen-ion concentration of the alkali solution is scarcely affected.

The other curve in Fig. 1, which represents the titration of beryllium sulphate, has two distinct sections in the acid zone. Precipitation was delayed until the beginning of the second section had been reached, when 1·04 equivalents of sodium hydroxide had been added. Thus the beryllium sulphate had to be rendered basic to the extent shown by the formula $BeSO_4,Be(OH)_2$, before a precipitate began to separate. Although the beryllium sulphate had become so basic, the solution remained perfectly clear and betrayed no sign of colloidality. Calculation from the analytical data of Parsons (*J. Amer. Chem. Soc.*, 1904, **26**, 1433) for the liquid phases saturated with respect to basic beryllium sulphate reveals that the liquid phases all contained soluble basic sulphate whose composition appeared to be independent of the concentrations used, *viz.*, from 0·38 to 2·86% of beryllium oxide. The average ratio of beryllium oxide to sulphate in twenty-two liquid phases was $BeO,0{\cdot}547SO_3$, the ratio appearing to have varied haphazardly from 0·508 to 0·622 mol. of SO_3. (In making these calculations the analyses of two liquid phases were discarded, for it seemed certain that the solutions could not have attained anything approaching equilibrium.) Parsons' solution thus contained a little less beryllium hydroxide than was the case with this solution while undergoing titration. The fact that there was a marked inflexion in the hydrion curve just at the stage when the first half of the stoicheiometric amount of sodium hydroxide had been added seems to indicate some fundamental difference between the first and second hydroxyl groups of beryllium hydroxide which gives rise to the formation of soluble basic salts in which the first beryllium valency is attached to the weaker hydroxide group. It must be stated, however, that concentrated solutions of beryllium sulphate can be rendered still more basic to the extent of 2 mols. of $Be(OH)_2$ to 1 mol. of $BeSO_4$. It is probable, whether the basic sulphate does or does not exist in solution as a definite chemical compound, that the solution is mainly colloidal in nature, in spite of the fact that it is clear and is not coagulated by electrolytes. The colloidal aggregates of beryllium hydroxide which probably exist in some type of combination with the sulphate groups appear to be capable of ionisation, although to a less extent than would have been the case had the sulphate radicals been united with beryllium simply. If these basic solutions happen to be examples of colloidal electrolytes, it would be expected that the dissolution of beryllium hydroxide in a beryllium sulphate solution, being

brought about by the formation of aggregates of the beryllium hydroxide and the beryllium sulphate, would be accompanied either by a diminution in the number of osmotically active particles, partly present as an ionisable colloid and partly in true solution, or, in the extreme and improbable case, by no change in the number. Some support for this view is to be found in the observations of Parsons, Robinson, and Fuller (*J. Physical Chem.*, 1907, **11**, 651), who found that the effect of dissolving beryllium hydroxide in solutions of beryllium sulphate was to raise the freezing point and to reduce the conductivity.

Precipitation of beryllium hydroxide was complete when 1·91 equivalents of sodium hydroxide (= 42·5 c.c.) had been added, the precipitate containing therefore $BeO,0{\cdot}045SO_3$. The contents of the solid phases obtained by Parsons (*vide supra*) in his study of the 25°-isotherm of the ternary system $BeO–SO_3–H_2O$ show that they contained between 0·034 and 0·048 mol. of SO_3 to each mol. of BeO.

The re-solution of the beryllium hydroxide was not complete when 90 c.c. of alkali had been added, which amount was a little in excess of that required to form sodium beryllate, Na_2BeO_2, neither did the titration curve give any indication that combination had taken place.

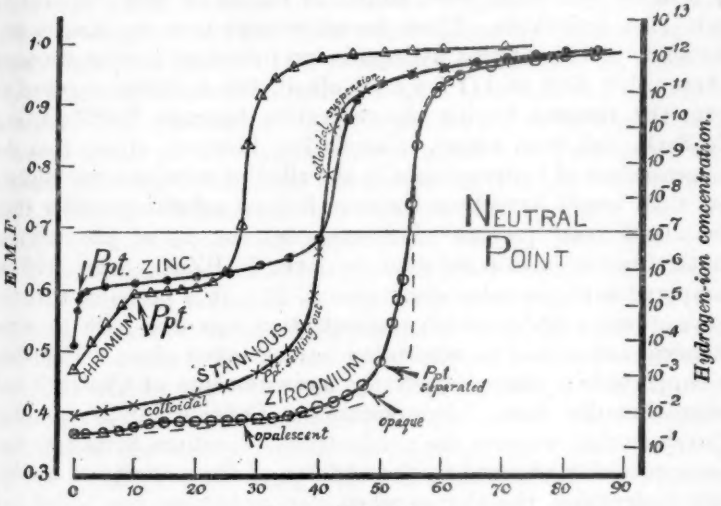
Hydroxides of Zinc, Chromium, Bivalent Tin, and Zirconium.—The titration curves are given in Fig. 2 and the particulars of the solutions in the following table. The temperature was 18°.

Soln. titrated (100 c.c.).	Normality of NaOH.	C.c. of NaOH theoretically required.	Precipitate first appeared. *E.M.F.*	p_H.	C.c. of NaOH.
0·025*M*-$ZnSO_4$	0·090	55·55	0·583	5·20	0·6
0·005*M*-$Cr_2(SO_4)_3,K_2SO_4$ (violet)	0·100	30·0	0·591	5·34	10·0
0·020*M*-$SnCl_2$	0·0932	42·9	—	—	—
0·01*N*-HCl ..... and	0·090	HCl = 11·1	Opalescent at 0·390	1·86	27·5
0·01*M*-$ZrCl_4$	—	Total = 55·5	Ppt. at 0·444	2·79	47·5

The curve representing the precipitation of zinc sulphate with sodium hydroxide shows that a basic sulphate was obtained. Precipitation was complete when 1·53 equivalents of alkali had been added, which may have been due to the separation of a basic sulphate, $ZnSO_4,3ZnO$. Pickering (J., 1907, **91**, 1981), who found that precipitation was complete and the solution had become alkaline to phenolphthalein when 1·59 equivalents of alkali had been added, concluded that the basic sulphate $ZnSO_4,4ZnO$ had been produced. As in other cases, the amount of alkali required was determined by the rate at which it was added, it appearing to be a rule that

the more slowly the alkali is added the less basic is the precipitate; this, once formed, is decomposed slowly by further additions of alkali. This no doubt accounts for the greater amount of alkali required by Pickering. It is almost certain that the precipitate formed does contain at least one definite basic salt, but the evidence at present available is insufficient to establish its individuality. Of the basic sulphates which have been described, that, with varying water contents, suggested by the titration seems to be the one described by the majority of workers, among whom may be mentioned Graham (*Phil. Trans.*, 1837, **127**, 47).

FIG. 2.



Sodium hydroxide began to produce a precipitate from zinc sulphate solution at p_H 5·2. It was shown in Part I that the solubility products of magnesium and manganous hydroxides calculated from the titration curves compare satisfactorily with those given by other methods, in spite of the fact that the precipitates actually obtained are basic. If the method be applied to the zinc titration, a value is obtained which is considerably at variance with the recorded values. Thus the extrapolated *E.M.F.* at 18° = 0·600 volt, therefore $p_H = 5{\cdot}48$, and the extrapolated amount of 0·090*N*-sodium hydroxide = 0·8 c.c., therefore $C_{Zn^{\cdot\cdot}} = 3{\cdot}6 \times 10^{-4}$, and consequently $[Zn^{\cdot\cdot}][OH']^2 = 10^{-21}$ approx. The values so far recorded are those by Herz (*Z. anorg. Chem.*, 1898, **23**, 227) and Bodländer (*Z. physikal. Chem.*, 1898, **27**, 66), who found the solubility of zinc hydroxide to be 2·6 and $2{\cdot}5 \times 10^{-5}$ gram-mol. per

litre respectively, from which the respective solubility product 1·8 and 1·6 × 10^{-14} are obtained. These values appear to b incorrect, for if correct they would correspond to a hydrogen-ion concentration of about 10^{-9} at which zinc hydroxide would b precipitated, as is the case with manganous hydroxide, whos solubility product is 1·3 × 10^{-14}. It will be shown in a later pape dealing with the precipitation of basic zinc salts—chromates carbonates—that such a hydrion concentration could not possibly be correct.

Complete re-solution of the zinc hydroxide did not take place in the course of the titration, although more than two molecules of sodium hydroxide were added in excess of that required to form zinc hydroxide. These measurements give no insight into the acidic nature of zinc hydroxide, no inflexions having appeared when either 83·3 or 111·1 c.c. of alkali, the amounts required to form the zincates having the respective formulæ $NaHZnO_2$ and Na_2ZnO_2, had been added. Calculation, however, shows that the concentration of hydroxyl-ions in the alkaline solutions was slightly less than would have been the case had no substances other than the alkali been present. For example, the p_H of the solution containing the alkali required to form $NaHZnO_2$ was 12·06 as compared with the calculated value 12·25. It is probable that the diminution in hydroxyl-ion concentration was due both to some chemical action and to adsorption having taken place. This view is supported by the conductivity measurements of Chatterji and Dhar (Faraday Soc., "Symposium on Colloids," 1921, p. 123), who state that whereas the conductivity of sodium hydroxide was not appreciably changed by the addition of the majority of amphoteric hydroxides, the change when zinc hydroxide was added was pronounced. Similar observations were made by Carrara and Vespignani (*Gazzetta*, 1900, **30**, 35) with potassium hydroxide solutions of zinc hydroxide. Hildebrand and Bowers (*J. Amer. Chem. Soc.*, 1916, **38**, 785) studied with the hydrogen electrode the reaction of alkalis with certain zinc salts and they claim to have obtained distinct evidence of the existence of monobasic zincic acid, $HHZnO_2$, for they found a sudden increase in p_H at the point where the amount of sodium hydroxide added was that required for the formation of $NaHZnO_2$. Repeated titrations have been made by the author on zinc salt solutions of the concentration used by Hildebrand and Bowers, but hitherto their observation has not been confirmed. It is interesting to recall that since Hildebrand and Bowers's paper appeared Goudriaan (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 179) has investigated the isotherm at 30° of the ternary system Na_2O–ZnO–H_2O and has found that

the only salt of sodium and zinc hydroxides is $Na_2ZnO_2,4H_2O$, which happens to exist in equilibrium with concentrated sodium hydroxide solutions containing from 27·8 to 39·2% of Na_2O. This salt is decomposed by water and so are the liquid phases with which it exists in equilibrium, for on dilution they deposit zinc hydroxide.

Chrome alum was chosen for the titration of the chromium salt, as it dissolves to give the normal violet solution. No precipitate was formed until one-third of the stoicheiometric amount of sodium hydroxide had been added—the p_H having previously rapidly increased until the precipitation p_H had been reached. The amount of alkali required to cause the beginning of precipitation seems to suggest that the basic salt retained in the solution had the formula $Cr(OH)SO_4$. It is probably a coincidence, for dissolved chromium sulphate can be rendered more basic and still remain in solution. The curve shows that the mother-liquor became alkaline when 27·5 c.c. (= 5·5 equivalents) of alkali had been added—an amount pointing to the final composition of the precipitate being $Cr_2O_3,0·25SO_3$. Williamson (*J. Physical Chem.*, 1923, **27**, 384) found, by adding varying amounts of sodium hydroxide to a decimolar solution of chrome alum, that when from 2 to 5 equivalents of alkali are added to one molecule of chrome alum the precipitates are almost constant in composition, $Cr_2O_3,0·7SO_3,3·6H_2O$, but when 6 equivalents are employed the precipitate is still more basic, as shown by the formula $Cr_2O_3,0·28SO_3,3·18H_2O$. This formula is similar to that indicated by the titration. Thus it appears that during the steady increase in p_H occurring while from 10 to 22 c.c. of alkali were being added a basic sulphate of approximately constant composition was being formed, which after precipitation became more hydrolysed by the further addition of alkali.

The titration curve affords no evidence of the constitution of alkaline solutions of chromium hydroxide, although the amount of alkali which was added was in excess of that required to form Na_3CrO_3. The amount of alkali was insufficient to dissolve the chromium hydroxide. The potential differences obtained in the alkaline solutions pointed to hydroxyl-ion concentrations which were a little less than those obtained by calculation. The difference may probably be accounted for by adsorption by the chromium hydroxide or possibly by some little union having taken place. Fricke and Windhausen (*Z. anorg. Chem.*, 1924, **132**, 273) also have shown that there is a slight difference in hydroxyl-ion concentration observable between sodium hydroxide solutions and those of chromium hydroxide in sodium hydroxide of the same concentration when measured by the Hg|HgO electrode.

Electrometric titrations were now carried out on violet and green solutions of chromium salts to see if some clue to the difference of colour could be discovered. The Werner co-ordination theory is generally held to give the most plausible explanation of the violet and green forms. Werner and Gubser (*Ber.*, 1901, **34**, 1579) first applied the theory to chromium chloride, and quite recently Lamb and Fonda (*J. Amer. Chem. Soc.*, 1921, **43**, 1154) referred to its application to chromium salts as "perhaps the most striking exemplification of the Werner theory of molecular structure." It is therefore surprising that the evidence on which Werner and Gubser based their views is quite unconvincing, and indeed, the difference might well be due to the existence in the green solutions of basic aggregates which are essentially colloidal in nature. The low conductivity of solutions of the green form of chromium chloride was regarded as evidence of the dissociation of a binary salt, $(CrCl_2,4H_2O)Cl,2H_2O$. The abnormal molecular weights calculated from the depression of the freezing point were supposed to supply fundamental evidence for this structure of the green form, for they happened to be of the order of one-half the molecular weight of hexahydrated chromium chloride. It is strange that the weight of six molecules of water should have been included in the latter molecular weight, seeing that four molecules only are supposed to be present in the nucleus of the complex chromium kation. The observed molecular weights of the violet chromium chloride were of the order of one-quarter of that of the hexahydrated salt, and this was taken as being due to $(Cr6H_2O)Cl_3$. The results show, however, that the observed molecular weights of the violet chloride in the more dilute solutions are somewhat too high—this may be regarded as due to incomplete ionisation—but it is surprising to find that the agreement between the observed and the theoretical values becomes perfect for a 12% solution, in which the dissociation must be far from complete. Werner and Gubser tried to confirm the view that only one chlorine atom in the green form was ionisable and therefore precipitable with silver nitrate, but always found that the amounts precipitated were greater than that corresponding to one atom, even in rapid estimations carried out at 0°. Similar observations have also been made on the incomplete precipitation with barium chloride from green chromium sulphate solutions. It is difficult to reconcile with the co-ordination theory the observations of Weinland and Koch (*Z. anorg. Chem.*, 1904, **39**, 296) on the precipitability of chlorine from green chromium chloride solutions with various silver salts, both in presence and in absence of free acid. The amount of chlorine precipitated depended on the nature and the quantity of the

particular silver salt used; without the addition of acids, all the silver salts precipitated at least two-thirds of the chloride. The presence of nitric acid had the effect of diminishing the amount of chloride liberated, whereas the silver salts of weak acids, such as acetic, lactic and nitrous, and silver sulphate immediately precipitated all the chloride. Silver salts of strong acids did not cause complete precipitation and free strong acids suppressed the precipitation even more. Lamb (*J. Amer. Chem. Soc.*, 1906, **28**, 1710; Lamb and Fonda, *ibid.*, 1921, **43**, 1154) tried to explain the above observations by a gradual transition from the green variety to the violet due to the hydrogen-ion concentrations ruling during the reactions, but in order to show how the transformation took place they found it necessary to postulate further that the green variety first underwent hydrolysis to form some such basic complex as $CrCl_2OH$.

The essential difference between the violet and the green salts of chromium appears to be concerned with the amount of hydrolysis and with a change in the chromium hydroxide which is probably akin to that produced by ageing. The normal or violet salts must therefore be prepared under such conditions that the hydrolysis is minimised by crystallising at as low a temperature as possible from very strongly acid solutions. The simplest way to convert the violet form into the green is by boiling. By so doing, the hydrolysis becomes enhanced and it is probable that the chromium hydroxide bound in the form of aggregates of basic salt tends to lose its reactivity. The change also seems to be linked up with the treatment to which the chromium hydroxide had been subjected previous to its solution in acids, for, as shown by Recoura (*Compt. rend.*, 1895, **120**, 1337), the change from violet to green can be effected by allowing an alkali solution of chromium hydroxide to age before dissolution in acid. It has been shown that the change in colour of chromium sulphate solutions is accompanied by the liberation of acid (see Denham, *Z. anorg. Chem.*, 1908, **57**, 361—bibliography given) with the consequent separation of a soluble basic salt. The dialysis experiments of van Cleeff (*J. pr. Chem.*, 1881, **23**, 58) and Richards and Bonnet (*Proc. Amer. Arts Sci.*, 1903, **39**, 1) show that the soluble basic aggregates are colloidal in nature, for the residue left in the dialyser from green solutions was basic whereas violet chromium sulphate passed through completely. Again, Richards and Bonnet have shown that in the precipitation of sulphate as barium sulphate from green sulphate solutions green basic chromium sulphate was always carried down.

The fact that barium chloride and silver nitrate produce incomplete precipitation appears to be a property in common with other

elements which give solutions which are almost certainly colloidal. Thus the chloride in ferric oxide hydrosols is not readily precipitated with silver nitrate, neither is it completely precipitated from solutions of either ferric or zirconium chloride in the cold, and especially after the solutions have been allowed to stand or have been boiled.

The change of violet solutions to green immediately on the addition of a little alkali is significant. The green colour of the solution containing the soluble basic chromium salt is undoubtedly connected with the existence of the green chromium hydroxide in solution in the form of basic aggregates.

Hydrogen electrode titrations have been carried out at 18° of violet solutions of both the chloride and the sulphate, and also of green solutions which were prepared by boiling the normal solutions for 5 minutes and rapidly cooling to 18°. The initial readings are given in the following table.

Salt.	Conc.	Colour.	*E.M.F.* against *N*-calomel.	p_H.	% Hydrolysis.
Chloride.....	0·0133	Blue	0·467	3·19	1·62
	0·0133	Green	0·409	2·18	16·4
Sulphate.....	0·0050	Violet	0·467	3·19	2·16
(as chrome alum)	0·0067	Green	0·395	1·94	28·7

The percentage of hydrolysis has been referred to the total amount of combined acid. It will be seen that the effect of boiling for a short time was to increase the amount of hydrolysis more than tenfold. The titration curves are similar to that given by chromium sulphate (Fig. 2), with the exception that the sections prior to precipitation in the case of the green solutions are somewhat curved, owing to the neutralisation of the liberated acid, instead of being rectilinear as in the case of the violet or blue solutions. The following table gives the important features of these titrations.

	Precipitation began.			Precipitation complete.
Salt.	*E.M.F.*	p_H.	Equivs. of NaOH to 1 equiv. of Cr.	Equivs. of NaOH.
Blue $CrCl_3$	0·588	5·28	1·07	2·78
Green $CrCl_3$	0·586	5·25	1·43	2·85
Violet chrome alum	0·591	5·30	1·00	2·75
Green chrome alum	0·587	5·27	1·21	2·71

The table shows that in each case precipitation was dependent on the attainment of a hydrion concentration, p_H 5·3, and that precipitation began from those solutions which contained chromium in the normal condition when about one equivalent of sodium hydroxide had been added, whilst the green solutions did not yield precipitates until somewhat larger proportions of alkali had

been added. The greater amounts of alkali required in the latter case show that the change produced in the solutions on turning from violet or blue to green has rendered the chromium salts more resistant in their behaviour towards alkali.

It is probable that the basic chromium complexes which seem to be present in green solutions are "micellar" in structure and constitute a colloidal electrolyte in which the kations are composed of chromium hydroxide and varying amounts of acid radical, a portion only being ionisable, and may perhaps be represented thus:

$$\left[\mathrm{Cr}_{(x+y+1)}\begin{matrix}(\mathrm{OH})_{3x}\\ \mathrm{R}_{3y}\end{matrix}\right]\mathrm{R}_3 \rightleftharpoons \left[\mathrm{Cr}_{(x+y+1)}\begin{matrix}(\mathrm{OH})_{3x}\\ \mathrm{R}_{3y}\end{matrix}\right]^{\cdots} + 3\mathrm{R}',$$

x and y being indefinite. Some such arrangement as this would account for the slowness with which silver chloride and barium sulphate may be precipitated from the appropriate green solutions, and this is especially so when the chromium solutions happen to be basic, such as may be prepared from the basic glassy masses obtained by evaporating solutions of chromium salts to dryness. There appears to be a tendency for one-third of the combined acid in a chromium salt, *i.e.*, the amount corresponding to that which seems to be loosely combined and gives rise to the formation of the "soluble basic salt," to be driven off on evaporation. Thus a basic salt prepared in this way had a composition corresponding to $\mathrm{Cr(OH)SO_4}$ and gave in solution no precipitate with barium chloride; neither did it do so with ammonia except on boiling or keeping. The soluble basic complexes in the green solutions have some properties in common with chromium hydroxide. Chromium hydroxide which has been suspended in water and boiled, or has been allowed to stand, becomes difficultly soluble in acids, as is also the case with ferric hydroxide, slowly dissolving only in concentrated acid solutions. Hence it is evident why the acids present in Weinland and Koch's experiments did not immediately decompose the green salt and render the chloride available for precipitation, and why the acid actually retarded the precipitation by depressing the ionisation of the colloidal electrolyte. The conception of basic aggregates also supplies an explanation why it was only the silver salts of weak acids which caused nearly all the silver chloride to be precipitated. The first reaction taking place between the precipitant and the colloidal electrolyte is one of double decomposition, whereby the chloride anion of the chromium complex is replaced by the anion of a weak acid. This would diminish the hydrogen-ion concentration of the solution, which would therefore tend to approach the value requisite for the precipitation of

chromium hydroxide; the basic complexes would thus be rendered so unstable that the chloride radicals in them would become susceptible to reaction with the silver salt.

A qualitative comparison of the absorption spectra of solutions of equal concentrations of (*a*) violet chrome alum, (*b*) green chrome alum, and (*c*) violet chrome alum to which an excess of sodium hydroxide had been added, revealed that those of solutions (*b*) and (*c*) were similar. The main difference between (*a*) and (*b*) was that the very faint yellow band, 5750—5950 Å., in the former had become wider and more pronounced in the latter, 5660–6110 Å. There was also some absorption in (*b*) in the blue region extending up to 4840 Å.; that in (*a*) extended to 4530 Å. The spectra of (*b*) and (*c*) were identical over the short wave-lengths, but the yellow band was found to have moved a little, to 5800–6160 Å. It is probable that alkaline solutions of chromium hydroxide are largely colloidal, and the similarity of the last two spectra would suggest that some part of the green solution also was colloidal, in which case the increased absorption might be attributed to the presence of exceedingly small colloidal basic aggregates.

The stannous chloride solution used in the titration shown in Fig. 2 was turbid and became more and more so until 30 c.c. of alkali had been added, when a heavy precipitate began to settle; the precipitate passed back again into colloidal suspension as soon as the solution had become alkaline ($p_H = 8{\cdot}7$) and 41·0 c.c. of sodium hydroxide had been added. From the *E.M.F.* readings made during the titration, the amounts of hydrolysed hydrochloric acid have been calculated at the various stages, from which the compositions of the basic stannous chloride aggregates given in the following table have been calculated.

C.c. of 0·0932*N*-NaOH.	*E.M.F.*	Atoms of Cl neutralised.	Fraction of unneutralised HCl hydrolysed.	Comp. of basic stannous chloride. To 1 atom of Sn. Cl.	OH.	Mol. of HCl hydrolysed.
0	0·391	0	0·336	1·33	0·67	0·67
5·1	0·401	0·24	0·269	1·29	0·71	0·47
10·0	0·412	0·47	0·208	1·22	0·78	0·32
15·2	0·418	0·71	0·204	1·03	0·97	0·26
20·0	0·428	0·93	0·173	0·88	1·12	0·18
25·15	0·440	1·18	0·145	0·63	1·37	0·12
30·0	0·463	1·40	0·085	0·55	1·45	0·05
35·0	0·499	1·63	0·033	0·36	1·64	0·01
39·0	0·585	1·82	0·002	0·18	1·82	0·0004

The table shows that the basic stannous chloride particles varied in composition from $SnCl_{1{\cdot}33}(OH)_{0{\cdot}67}$ to $SnCl_{0{\cdot}55}(OH)_{1{\cdot}45}$ during the addition of the 30 c.c. of alkali and yet remained in colloidal suspension. The last column indicates that the molecular proportion

of hydrochloric acid hydrolysed gradually grew less as the titration proceeded. It was not until the particles had become to this extent basic, and the concentration of the free hydrochloric acid with which they had existed in equilibrium had become relatively small, that the colloidal solution coagulated. The solution became neutral when 40 c.c. of alkali had been added, showing that chloride was still being retained by the stannous hydroxide, its composition having then become $SnCl_{0\cdot14}(OH)_{1\cdot86}$. The fact that peptisation of the precipitate took place immediately the mother-liquor became alkaline seems to be important, and it may be that the reaction of the alkali with the retained chloride in the precipitate was largely responsible. No inflexion was produced in the curve in the alkaline zone.

Hildebrand (*loc. cit.*), besides finding an inflexion for zinc hydroxide, found one for zirconium hydroxide also. The precipitation of zirconia from a solution in hydrochloric acid has been investigated (Fig. 2) and also the change in p_H in the mother-liquor when the precipitated zirconium hydroxide was in presence of an excess of sodium hydroxide. The present experiments fail to confirm Hildebrand's observation of a distinct inflexion, which he stated to correspond to the formation of sodium zirconate. There appear to be absolutely no grounds for regarding zirconium hydroxide as amphoteric. Unlike the other hydroxides studied in this paper, that of zirconium is not dissolved by alkalis under any conditions. In common with all other gelatinous hydroxides, it adsorbs salts from solutions in which it may be suspended, and on precipitation with an excess of alkali does naturally adsorb some alkali, the amount depending on the quantity of alkali present. These precipitates do not hold the alkali in any form of combination, as would be the case if they contained insoluble zirconates. It is remarkable that whilst alumina is one of the few oxides which can be considered with any degree of certainty to be amphoteric in the wet state, it should be the only one which is definitely amphoteric in the dry state, yielding on fusion with alkalis or with alkali metal carbonates products which are soluble.

The titration curve gives some insight into the mechanism of precipitation. The hydrochloric acid solution was prepared from a basic zirconium chloride which contained 1·737 mols. of Cl to 1 mol. of ZrO_2. The basic chloride dissolved in water to give a perfectly clear solution. An aqueous solution, 0·04 normal with respect to the chloride content, was hydrolysed immediately after preparation to the extent of 54%. The dotted line in the diagram represents the neutralisation curve of hydrochloric acid solution having the same chloride concentration as that of the acid solution

of zirconium chloride with the same alkali solution. The small but definite inflexion which occurred when 11·1 c.c. of alkali had been added is remarkable. It marks the end of the neutralisation of the excess of acid over that required to form zirconium tetrachloride and thus points to the existence in solution of zirconium chloride, although considerably hydrolysed. This is opposed to the generally accepted view that the chloride dissolves as "zirconyl chloride," $ZrOCl_2$, dissociating into "zirconyl" ions, $ZrO^{\cdot\cdot}$, and Cl' and free hydrochloric acid. The solution began to become opalescent when 27·5 c.c. of alkali had been added, and this was before the amount of alkali had been added which was necessary to form either $ZrOCl_2$ (33·3 c.c.) or the basic salt from which the solution was prepared (36·2 c.c.). As solutions of both these substances happen to be perfectly clear, it follows that the premature opalescence obtained in the titration must have been due either to the electrolytes present or to the hastened growth of the colloidal particles owing to the rate at which the alkali was added. It must have been due to the latter, for salts may be added to basic zirconium chloride solutions of similar composition without producing any perceptible effect. The zirconium chloride curve tends to approach the hydrochloric acid curve when approximately two equivalents of sodium hydroxide have been added (33·3 c.c.). At this stage the chloride radicals in combination with the zirconium were undergoing the maximum hydrolysis. The solution became increasingly colloidal in appearance as the alkali was added until it became opaque and coagulation suddenly took place (47·5 c.c.). The following table gives the fraction which had suffered hydrolysis of the portions of zirconium chloride which had not entered into the reaction at the various stages in the titration, from which has been found the composition of the unhydrolysed basic zirconium chloride together with the molar proportion of the free acid which had been hydrolysed.

C.c. of NaOH.	*E.M.F.*	Atoms of Cl neutralised.	Fraction of unneutralised HCl hydrolysed.	Comp. of basic chloride. To 1 atom of Zr. Cl.	Comp. of basic chloride. To 1 atom of Zr. OH.	Mols. of HCl hydrolysed.	Remarks.
0	0·366	0	0·529	2·12	1·88	3·12	Free HCl
11·1	0·380	0	0·579	2·32	1·68	2·38	,,
22·2	0·386	1·0	0·670	3·01	0·99	2·01	Clear
27·8	0·390	1·5	0·714	3·28	0·72	1·78	Opalescent
33·3	0·393	2·0	0·828	3·66	0·34	1·66	,,
36·2	0·397	2·267	0·831	3·70	0·30	1·44	,,
38·9	0·406	2·5	0·685	3·53	0·47	1·03	,,
44·4	0·426	3·0	0·480	3·48	0·52	0·48	,,
47·5	0·444	3·28	0·333	3·52	0·48	0·24	Opaque
50·0	0·481	3·5	0·107	3·55	0·45	0·05	Coagulated
52·7	0·571	3·75	0·006	3·75	0·25	0·00	,,

In these calculations it has been assumed that the hydrochloric acid was completely dissociated. The degree of hydrolysis of the zirconium chloride in the free acid solution was obtained by subtracting the hydrion concentration produced by the excess of acid from the total hydrion concentration calculated from the observed voltage.

It will be seen that the maximum hydrolysis occurred when just over two atoms of chloride of the zirconium chloride had been reacted upon, and that the rapid increase in hydrolysis during the first portion of the titration was accompanied by a corresponding change in the composition of the basic zirconium chloride actually present in the solution (columns 5 and 6). Thereafter, the composition of the basic zirconium chloride remained nearly constant and corresponded roughly with the formula $Zr(OH)_{3\cdot5}Cl_{0\cdot5}$, until after coagulation ensued, when it was partially decomposed by the alkali. The first half of the titration, besides yielding a rapidly increasing basic chloride, was accompanied by a gradual decrease in the amount of free acid, which tended to render the basic zirconium chloride more and more insoluble and thus produced a gradual growth in the size of the basic chloride particles. At the beginning of the titration the particles probably approximated to molecular dimensions, but as the chloride became more and more basic these exceedingly small particles coalesced to form larger and larger aggregates until they became sufficiently big to render the solution opalescent, and this process still continued through the period when the solution had become visibly and increasingly colloidal right up to the point when coagulation occurred. The table shows that the free acid had some inhibiting effect on this growth in the size of the particles, for it was only after an appreciable proportion of the acid had been neutralised that the solution became opalescent, and, after the basic chloride particles had become uniform in composition, it was only after the amount of free acid had been almost removed that the colloidal solution coagulated.

These observations seem to suggest that the nature of basic zirconium salt solutions is essentially colloidal in spite of the fact that many of the solutions are perfectly clear. Müller (*Z. anorg. Chem.*, 1907, **52**, 316) arrived at the same conclusion from a study of the reactions of zirconium salt solutions. The observations, moreover, furnish an excellent example to show that the process of precipitation is one which involves the formation of a colloidal solution which subsequently coagulates. In the majority of precipitations the colloidal solution stage is so rapidly passed that it is not observed.

Adolf and Pauli (*Kolloid Z.*, 1921, **29**, 173) found that the hydrolysis of solutions of zirconium oxychloride, $ZrOCl_2$, of concentrations ranging from 0·0022 to 0·125*M*, after 10 days' standing, varied irregularly between 35 and 50%. As mentioned above, a freshly prepared solution of zirconium chloride containing 1Zr : 1·737Cl was hydrolysed to the extent of 54%, whereas in the solution containing the basic chloride having the same composition in the titration the hydrolysis was considerably greater, *viz.*, 83·1%. In the latter case, the solution was opalescent and therefore contained larger particles than the corresponding clear solution. Thus the degree of hydrolysis appears to be a function of the size of particle, and consequently the smaller amount of hydrolysis in the clear solutions of Adolf and Pauli must have been due to the presence of particles which had been rendered small by the solution effect of the free acid. They prepared zirconium oxide hydrosols by dialysis, which contained appreciable amounts of chloride; one contained 0·33 atom of chlorine and the other 0·26 atom to each atom of zirconium. Both sols were hydrolysed to small extents, *viz.*, 0·9 and 0·6%. It is important to note that, although the concentration of free acid was small, there was a relatively large concentration of chloride ions, 41 and 37% respectively of the total chlorine content. The ratio Zr : Cl in these hydrosols corresponds to points on the titration curve lying between those representing 3·5 and 3·75 equivalents of sodium hydroxide, *i.e.*, just after coagulation had taken place. The amount of free acid was of the same order in both the colloidal solutions and the mother-liquor in which the basic zirconium precipitate was suspended. The large concentration of chloride ions in the colloidal solutions shows that the basic chloride particles do dissociate in some way.

The degree of dispersion of colloidal basic chloride solutions appears to be dependent on the amount of acid present. Colloidal solutions of basic chloride in which some free acid is present tend to become clear on standing, no doubt owing to the tendency of the colloidal particles to pass into solution. This behaviour may possibly account for Rodd's observation (J., 1917, **111**, 396) that a basic chloride, $Zr_5O_8Cl_4,22H_2O$, separated at first from concentrated solutions of zirconia in which the concentration of hydrochloric acid had been suitably regulated. When the solution had become more acid owing to separation of the highly basic chloride, crystals of ordinary $ZrOCl_2,8H_2O$ began to separate. Rodd believed that the formation of the very basic chloride (Zr : Cl = 5 : 4) was due to some intrinsic change having taken place in the constitution of the zirconium hydroxide. The important point is

that the salt appears to have given a clear solution, whereas when the zirconium chloride present in the solution undergoing titration had acquired the same composition by the addition of 35·5 c.c. (= 3·2 equivalents) of sodium hydroxide the solution became opaque. Rodd mentions that a solution of his salt was precipitated by either sulphuric acid or sulphates generally. There seems to be no doubt that Rodd obtained his highly basic chloride through using a concentration of hydrochloric acid much less than that required for the crystallisation of the usual $ZrOCl_2,8H_2O$, and thus obtained a substance nearly as basic as that shown to exist in the solution during the second part of the titration, *viz.*, $Zr(OH)_{3\cdot5}Cl_{0\cdot5}$. Rodd's salt is $Zr(OH)_{3\cdot2}Cl_{0\cdot8}$. The fact that Rodd obtained his salt by a slow crystallisation process from an acid solution indicates that it must have been composed of very small particles, their growth having been prevented by the acid present. Hence the reason for the substance passing into a clear or nearly clear solution. The fact that sulphates in general caused its precipitation appears to be an example of the normal behaviour of electrolytes towards colloidal solutions. Rodd, however, believed these precipitations to be cases of double decomposition, as the precipitates obtained by the addition of sulphuric acid and ammonium sulphate were within a few units % of the same composition, $Zr_5O_8(SO_4)_2,14H_2O$. He was of the opinion that this formula represents a "true chemical individual," but added that there was "no evidence to show that this is a true hydrate."

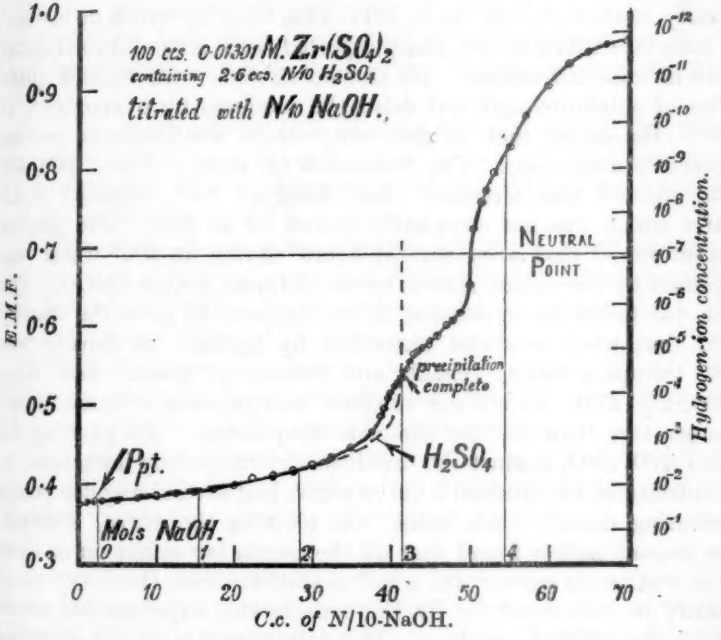
Solutions of zirconium sulphate behave towards some reagents in a manner quite different from that of solutions of either the chloride or the nitrate, so much so that Ruer (*Z. anorg. Chem.*, 1904, **42**, 85) and others have postulated that the sulphate must exist in solution as a complex zirconium sulphuric acid in which the zirconium is present in a complex anion and thereby escapes precipitation. Thus oxalic acid and alkali metal oxalates fail to precipitate it, and sulphites only precipitate it slowly and incompletely. If potassium chloride be added to a zirconium sulphate solution, either before or after the addition of sodium oxalate, the solution becomes readily precipitable. Another point of difference is the behaviour towards sodium tartrate. Zirconium chloride yields a precipitate with sodium tartrate, readily soluble in excess, as compared with the precipitate which is obtained from zirconium sulphate solution, which dissolves only on boiling or on prolonged standing. The precipitate in the latter case is mainly basic zirconium sulphate. Chauvenet (*Ann. Chim. Phys.*, 1920, **13**, 82) titrated several zirconium salt solutions conductimetrically and found that the titration curves, instead of being straight lines as

in acid–alkali neutralisations, were slightly curved, such that the tangents drawn to the curves at each end intersected at points corresponding to approximately two equivalents of alkali. This he claimed to be evidence for the existence of the "zirconyl," $ZrO^{\cdot\cdot}$, radical. The data given in the previous table show that during the addition of the first two equivalents of alkali the basic chloride undergoes hydrolysis and the remaining two equivalents cause little variation in its composition, $Zr(OH)_{3\cdot5}Cl_{0\cdot5}$, except at the end. These two processes, which took place in the precipitation from zirconium chloride solution, undoubtedly account for the change in the slope of Chauvenet's curve, which had therefore nothing to do with an alleged zirconyl radical. Chauvenet also titrated a solution of zirconium sulphate by the conductivity method and obtained the point of minimum conductivity when 3 equivalents of alkali had been added; this he claimed to be due to the separation of a definite basic sulphate, $ZrOSO_4,ZrO_2$. He also claimed that an inflexion was produced when two equivalents of alkali had been added, which pointed to another definite basic salt, zirconyl sulphate, $ZrOSO_4$. In view of the peculiar properties shown by zirconium sulphate and of the contentions of Chauvenet, it was decided to subject the sulphate to titration with the hydrogen electrode.

The zirconium sulphate had the composition $ZrO_2,2{\cdot}10SO_3,2{\cdot}29H_2O$, from which a 0·01301*M*-$Zr(SO_4)_2$ solution was prepared at room temperature; therefore 100 c.c. of the solution contained uncombined sulphuric acid equivalent to 2·56 c.c. of *N*/10-alkali. The curve showing the titration with *N*/10-sodium hydroxide of 100 c.c. of this solution at 18° is given in Fig. 3. The first inflexion occurred when the added alkali was equivalent to 3 mols. to 1 mol. of zirconium sulphate. At this point precipitation was complete and the solid had the composition $ZrO_2,\frac{1}{2}SO_3,xH_2O$. Further addition of alkali (up to 50·4 c.c.) caused its partial decomposition and the mother-liquor became alkaline. The precipitate must then have contained $ZrO_2,0{\cdot}16SO_3$, but, as the slope of the curve shows, during the addition of the next few c.c. of alkali some alkali was still being withdrawn from the solution and utilised in decomposing the precipitate still more. The sulphate solution, unlike that of the chloride, began to yield a precipitate immediately the alkali was added. It is curious that by warming zirconium sulphate solution it may be made strongly basic by means of alkali without the separation of a precipitate, the solution remaining quite clear. The dotted curve given in Fig. 3 is the titration curve of 100 c.c. of sulphuric acid containing 41·6 c.c. of *N*/10-sulphuric acid, equivalent in concentration to three-quarters of the com-

bined acid in the zirconium sulphate solution together with the small amount of free sulphuric acid. The two curves are nearly coincident over the first half of the zirconium sulphate curve, but vary a little during the addition of the third equivalent. The curves show therefore that the zirconium sulphate solution contained a basic sulphate and free sulphuric acid in approximately the proportions 1 mol. of $ZrO_2,\frac{1}{2}SO_3$ to $1\frac{1}{2}$ mols. of H_2SO_4. The addition of alkali had the main effect of neutralising the free sulphuric acid, with the consequence that the basic sulphate with which it had existed

FIG. 3.



in some kind of equilibrium was precipitated. The curves give no evidence of Chauvenet's so-called zirconyl sulphate, but do confirm his observation of the precipitation of a basic sulphate of approximately the composition $ZrO_2,\frac{1}{2}SO_3$. Further work, however, is necessary on the lines of the phase rule before its individuality can be established.

Chauvenet (*loc. cit.*) determined the molecular weight of zirconium sulphate from the depression of the freezing point of an aqueous solution, and found it to be a little more than a quarter of that of $ZrOSO_4,H_2SO_4$. He therefore argued that zirconium sulphate on solution split up into zirconyl sulphate and sulphuric

acid. If, however, the partial dissociation of sulphuric acid be taken into consideration, the anomalous freezing point might also be taken to support the constitution of zirconium sulphate solution suggested by the above titrations.

The view that these somewhat inert basic zirconium sulphate particles exist in solution in equilibrium with hydrolysed sulphuric acid gives an explanation of the abnormal behaviour of reagents towards zirconium sulphate solutions, especially that of sodium tartrate in precipitating the basic sulphate in such a state that it is not readily soluble in excess of the reagent.

Some criticism appears to be not out of place here of Chauvenet's density method (*Compt. rend.*, 1917, **164**, 864), by which he claimed to ascertain which of the many reported basic zirconium sulphates were definite individuals. He treated zirconia with various quantities of sulphuric acid and dried the products by evaporation at 200°. He stated that at this temperature the products became rigorously anhydrous. Van Bemmelen (*Z. anorg. Chem.*, 1906, **49**, 125) showed that zirconia, when dried at 200°, retained much water which was not completely driven off at 300°. The present author found that after several hours' drying at 200° water was retained to the extent shown by the formula $ZrO_2,0{\cdot}48H_2O$. The salt was found by immersion in nitrobenzene to have the density 4·02, but when rendered water-free by ignition its density was 5·47 (compare 5·489, Venable and Belden, *J. Amer. Chem. Soc.*, 1898, **20**, 273). Zirconium sulphate also requires a much higher temperature than 200° for complete dehydration. By plotting the ratio $ZrO_2 : SO_3$ against the densities, determined by immersion in nitrobenzene, he obtained a curve which had several angular points indicating definite basic salts. On plotting the curve, however, the present author found that all the points lay either on or close to a continuous curve; the small deviations from the curve could readily be accounted for by the considerable experimental errors which the method involved. The determination of the densities of amorphous substances, such as these basic sulphates, is a difficult problem, and the values at best can only be approximate on account of the difficulty of completely filling the porous particles with nitrobenzene. It is conceivable that Chauvenet's density method might be applied in cases where the densities, supposing they could be determined with sufficient accuracy, of the different basic salts were widely different. There is no agreement between Chauvenet's density of $3ZrO_2,4SO_3$, 3·02, and that, 4·1, of Hauser and Herzfeld (*Z. anorg. Chem.*, 1910, **67**, 369). It thus appears that the conclusions of Chauvenet are without satisfactory grounds.

Summary.

(1) The hydrogen-ion concentrations ruling throughout the precipitation of the hydroxides, actually basic salts, of aluminium, beryllium, zinc, chromium, stannous tin, and zirconium have been investigated.

(2) The hydrogen-ion concentrations to be attained for the precipitation of the hydroxides of aluminium, beryllium, zinc, and chromium have been found.

(3) New light has been thrown on the nature of the characteristic soluble basic salt solutions of beryllium, chromium, and zirconium.

(4) The manner of precipitation of stannous and zirconium hydroxides has been shown to be that of the formation and subsequent coagulation of a colloidal solution of dispersed basic chloride particles.

(5) It has been shown that of the bases studied in this paper aluminium hydroxide is the only one which is definitely amphoteric. No confirmation of the observations of Hildebrand on zirconium and zinc hydroxides could be obtained.

(6) The study of zirconium chloride and sulphate solutions has revealed that both are composed of highly dispersed basic particles and hydrolysed acid. No evidence could be obtained of the existence of the " zirconyl " radical.

(7) The hydrogen-ion concentration of precipitation of zinc hydroxide (actually basic sulphate) has been shown to be not in accord with the recorded solubility product data.

(8) It has been shown that the Werner co-ordination theory does not give a satisfactory explanation of the anomalous behaviour of green chromium chloride and sulphate solutions.

In conclusion, the author takes this opportunity to thank Prof. J. C. Philip, F.R.S., for facilities in carrying out this work, the Chemical Society for a grant for the purchase of salts of the rarer metals, and the Department of Scientific and Industrial Research for a personal grant.

Imperial College of Science and Technology,
South Kensington. [*Received, June 20th*, 1925.]

CCLXXXIX.—*Electrometric Studies of the Precipitation of Hydroxides. Part III. Precipitation in the Cerite Group of Rare Earths and of Yttrium Hydroxide by Use of the Hydrogen Electrode.*

By Hubert Thomas Stanley Britton.

The precipitation of the hydroxides of the metals of the "cerite" group and of yttrium has been investigated by means of titrations with the hydrogen electrode. The solutions used and the hydrogen-ion concentrations at which the various precipitations began are given in the table.

Titration and curve No.	Temp.	Solution titrated (100 c.c.).	Normality of NaOH.	Theor. amount of NaOH. (C.c.).	Precipitation began. *E.M.F.*	p_H.	C.c. of NaOH.
1	17°	0·0133*M*-$La(NO_3)_3$	0·090	44·4	0·763	8·35	1·0
2	17	0·0133*M*-$CeCl_3$	0·1018	39·0	0·709	7·41	1·8
3	17	(1) 0·0163*N*-HCl	0·1018	16·0			
		(2) 0·0114*M*-$PrCl_3$		33·6	0·690	7·05	18·2
4*a*	17	0·0133*M*-$Nd(NO_3)_3$	0·1018	39·0	0·686	7·00	0·8
4*b*	17	(1) 0·0154*N*-HCl	0·1018	15·1			
		(2) 0·0114*M*-$NdCl_3$		33·6	0·687	7·02	18·0
5	18	0·0133*M*-YCl_3	0·090	44·4	0·674	6·78	1·0
6	18	(1) 0·0140*N*-HCl	0·1018	13·75			
		(2) 0·0121*M*-$SaCl_3$		35·53	0·676	6·83	16·1

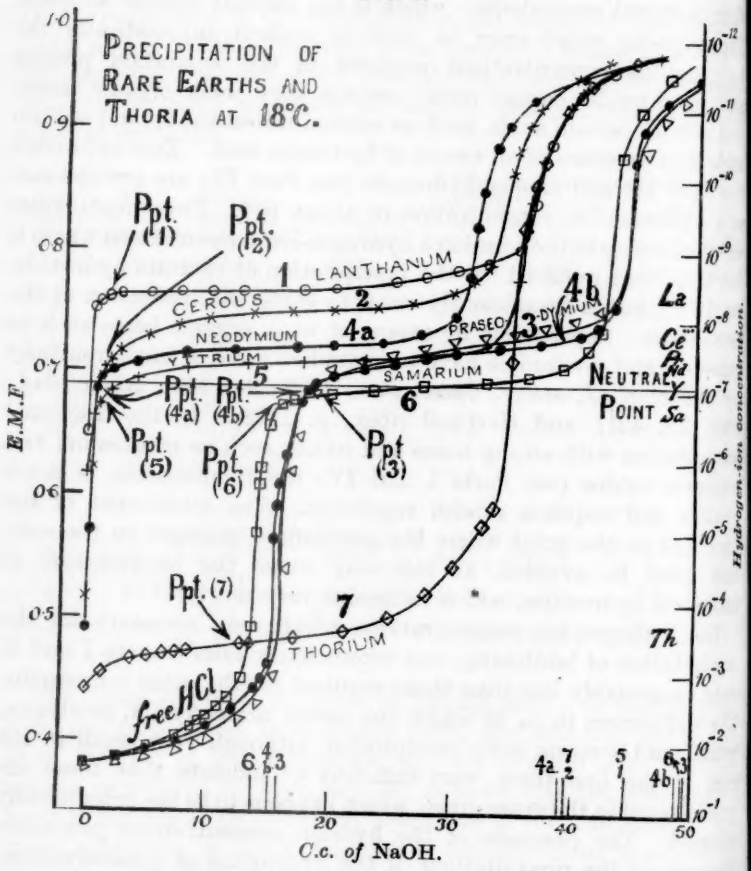
The titration curves are given in the diagram. As thoria occurs with the rare earths in monazite sand, the titration curve (No. 7) of 100 c.c. of 0·01*M*-thorium chloride solution with 0·1016*N*-sodium hydroxide has been included in order that the precipitation p_H of thoria might be compared with those of the rare earths. The great difference in the hydrogen-ion concentrations accounts for the ease with which thoria can be separated from the rare earths of the "cerite" group by those methods which depend on the change in p_H. Knowing the respective hydrion concentrations it is possible to effect the separation of thorium hydroxide from the rare earths by carefully varying the p_H of the solution by means of alkalis and suitable indicators. The hydrogen-ion concentrations may be varied: (*a*) by using reagents which impart hydrion concentrations to the solutions greater than those to be attained for the precipitation

of the rare earths but less than that for thorium hydroxide, and (*b*) by fractional precipitation with bases which produce p_H's which are greater than those produced by the bases to be separated. Methods employing the former device need no control, but those based on the latter principle must be controlled, either as regards the hydrion concentrations by means of indicators or electrometric measurements, or as regards the fractions themselves by determining their chemical equivalents; which is the method usually adopted. The reagents which may be used to control automatically the hydrogen-ion concentrations required in the separation process are: zinc oxide, copper oxide, certain very weak organic bases, and salts of certain acids, such as sodium thiosulphate, and sodium azide if in presence of an excess of hydrazoic acid. Zinc hydroxide (see Part II) and copper hydroxide (see Part IV) are precipitated at a hydrogen-ion concentration of about 10^{-6}. These hydroxides will thus set up in the solution a hydrogen-ion concentration which is less than that required for the precipitation of thorium hydroxide, *viz.* $10^{-3\cdot6}$, but is insufficiently small to cause the separation of the rare earths. Separations by means of weak organic bases such as quinoline and *p*-toluidine have been studied more or less empirically by Jefferson (*J. Amer. Chem. Soc.*, 1902, **24**, 540), Allen (*ibid.*, 1903, **25**, 421), and Hartwell (*ibid.*, p. 1128). In the fractional precipitation with strong bases and oxides such as magnesium and mercuric oxides (see Parts I and IV) the fractionation is much quicker and requires careful regulation. The attainment of too high p_H's at the point where the precipitant impinges on the solution must be avoided, as this may cause the precipitation of undesired hydroxides, which redissolve very slowly.

The hydrogen-ion concentrations which were necessary for the precipitation of lanthanum and cerous hydroxides (curves 1 and 2) were appreciably less than those required for the other four earths. The differences in p_H at which the earths praseodymia, neodymia, yttria, and samaria were precipitated, although very small in the case of the first three, were sufficient to indicate that these are precipitated in the order given, which happens to be the order usually claimed. The closeness of the hydrion concentrations prevailing throughout the precipitations of the hydroxides of praseodymium, neodymium, and yttrium shows that a separation of these three earths by a hydrogen-ion concentration method is impracticable. The strongest base of the yttrium group is generally stated to be yttria, and according to these measurements, it appears to have a strength of the order of that of "didymia." Curves 4*a* and 4*b*, illustrating the respective titrations of the nitrate and chloride of neodymium, show, contrary to the observations of Hildebrand

(*J. Amer. Chem. Soc.*, 1913, **35**, 847), that the hydrogen-ion concentration required for the precipitation of neodymium hydroxide is quite independent of the nature of the anion. Hildebrand found that the p_H value required for precipitation from a chloride solution lay between 7 and 8, but from a nitrate solution between 4 and 5. The lower value obtained for the nitrate solution must have been

FIG. 1.



due to the use of an electrode whose hydrogen was catalytically reducing the nitrate. It has always been found, however, that when such reduction was taking place the *E.M.F.*'s were far from stationary.

In none of these titrations was the pure hydroxide obtained, as is shown by the following amounts (equivalents) of alkali which caused complete precipitation: from lanthanum nitrate solution,

2·60; cerous chloride, 2·61; praseodymium chloride, 2·45; neodymium nitrate, 2·38; neodymium chloride, 2·53; yttrium chloride, 2·36; and samarium chloride, 2·48.

The separation of basic lanthanum nitrate is yet another example in which the course of precipitation can be followed through the transitional colloidal stage. On the addition of 1·6 c.c. of sodium hydroxide the solution became opalescent. During the addition of the first 35 c.c. of alkali (=2·37 equivalents) there was a gradual increase in p_H from 8·35 to 9·0, which did not cause the separation of a precipitate, for the lanthana passed continuously into the colloidal state, shown by an increasing turbidity of the solution. The next 2·5 c.c. caused a rapid diminution in the hydrion concentration, which was accompanied by a rapid increase in turbidity, whilst the next c.c. caused the solution first to become opaque and then to coagulate completely. The hydrion concentration had then become $10^{-10·9}$, a value considerably less than that required for the precipitation of lanthana. The amount of alkali required shows that the composition of the precipitate was given by $La(OH)_{2·6}(NO_3)_{0·4}$, indicating, as in other instances, that the dispersed particles were basic. The sudden fall in the hydrion concentration towards the end of the reaction was caused by an excess of alkali having passed into the mother-liquor, and must have been due to the action of this alkali on the colloidal particles which ultimately brought about the coagulation of the colloidal solution.

If the order of the precipitation of the hydroxides is actually that of their basic strengths, the basic strengths of the rare earths here investigated lie between those of zinc and manganous hydroxides, and below that of magnesium hydroxide. Lanthanum hydroxide is always stated to be the strongest base of the rare earths, and the "cerite" group of hydroxides, excepting ceric hydroxide, to be the group of the strongest bases. Apart from lanthanum hydroxide and perhaps cerous hydroxide, the other earths appear to be quite moderate in strength and are comparable with cobalt and nickel hydroxides. This is contrary to the view generally held. Friend ("Text Book of Inorganic Chemistry," 1917, Vol. IV, p. 257) states that "from general chemical and thermochemical considerations it may be concluded that they [the rare earths] are stronger than magnesia, but weaker than the alkaline earths." The chemical considerations are epitomised thus: "The strongly ignited oxides are readily soluble in mineral acids, several of them combine directly with water and absorb carbon dioxide from the air, and all of them liberate ammonia from cold solutions of ammonium salts. Normal salts of numerous weak acids, *e.g.*, chromic, carbonic, are readily prepared." If the hydrogen-ion concentration relationships do

give the true order of basic strengths, then zinc hydroxide is a weaker base than either of the tribasic hydroxides of the "cerite" elements, yet its oxide after ignition is readily soluble in mineral acids. The behaviour of the rare earths towards cold ammonium salt solutions is misleading. The fact that a base forms well-defined salts with weak acids probably offers no clue to its strength, if those salts happen to be almost insoluble. This is the case with the carbonates and chromates of the rare earths (*vide* Britton, J., 1924, **125**, 1873). Thus thorium hydroxide is an exceedingly weak base, but under certain conditions it forms an extremely well-defined chromate; under other conditions it behaves like other weak bases and gives precipitates which are indefinite and basic (*vide* Britton, J., 1923, **123**, 1429). The power to form well-defined salts with weak acids seems to be a property inherent in an element in conferring a small solubility on a salt and probably has nothing whatsoever to do with its power to form a strong base. There is no marked difference in the stability of soluble acetates and that of the acetates of the metals whose hydroxides are precipitated at comparable hydrogen-ion concentrations, *e.g.*, zinc, cobalt, nickel, and cadmium.

Vesterberg found (*Svensk. Kemi Tidskrift*, 1917, **29**, 101; *Zeitsch. anorg. Chem.*, 1917, **99**, 11, 22) that equally concentrated solutions of lanthanum acetate and ammonium acetate were equally hydrolysed. This led him to conclude hat the strengths of lanthanum hydroxide and ammonium hydroxide are nearly the same. The titration shows that lanthana was precipitated from an alkaline solution the hydrogen-ion concentration of which varied from $10^{-8\cdot35}$ to 10^{-9}. The very small concentration of lanthanum hydroxide therefore imparts to the solution a hydroxyl-ion concentration of the order of 10^{-5}, a concentration which is restricted by the small solubility of the lanthana. The actual amount of dissolved lanthanum hydroxide is too small for accurate estimation, and consequently it is not possible to calculate its degree of dissociation and its basicity constant, nor to compare the hydroxyl-ion concentrations given by equal concentrations of ammonia and lanthana. Theoretically it is possible to compare them from a knowledge of the degrees of hydrolysis of solutions of their respective salts under absolutely identical conditions. It is extremely doubtful whether this is accomplished by Vesterberg's method on account of the different nature of the two bases, for on extracting the hydrolysed acid from a lanthanum acetate solution with ether the equilibrium is disturbed in some unknown manner. The lanthanum hydroxide, unlike the ammonium hydroxide in the case of the ammonium acetate solution, will tend to become precipitated or to pass into colloidal solution, and thereby give rise to increased hydrolysis.

The hydrogen-ion concentrations at which lanthanum and cerous hydroxides are precipitated are a little greater than that necessary for manganous hydroxide. It was therefore thought that the presence of ammonium chloride in sufficient quantity might prevent their precipitation with ammonium hydroxide (see Part I). Calculation shows that, for each molecule of ammonia, 14 and 32 molecules, respectively, of ammonium chloride should be sufficient to prevent the precipitation of lanthanum hydroxide and cerous hydroxide. Actually, ammonium chloride has some inhibiting effect on the precipitation of the two hydroxides, and when the proportion of ammonium chloride to ammonium hydroxide is large, as indicated by the calculations, the precipitation can be entirely prevented.

Summary.

Hydrogen electrode titrations of solutions of several rare-earth salts with sodium hydroxide show that:

(*a*) The order of the precipitation of the earths with alkali is samarium, yttrium, neodymium, praseodymium, tervalent cerium, and lanthanum.

(*b*) The hydrogen-ion concentrations which govern the precipitation of the hydroxides of samarium, yttrium, neodymium, and praseodymium are so very close to one another—all about 10^{-7}—that the separation of these hydroxides by fractional precipitation is not possible.

(*c*) The precipitate formed in each titration is basic.

(*d*) The precipitation p_H's of the rare earths lie below those of magnesium and manganous hydroxides and above that of zinc.

(*e*) The great difference between the hydrion concentration necessary for the precipitation of thorium hydroxide and those required in the case of the rare earths accounts for some of the processes which are used to effect its separation.

(*f*) Ammonium chloride, if present in sufficient quantity, prevents the precipitation of lanthanum and cerous hydroxides.

The author avails himself of this opportunity to thank Prof. Philip, F.R.S., for facilities in carrying out this work, the Chemical Society for a grant which covered the cost of the materials, and the Department of Scientific and Industrial Research for a personal grant.

Imperial College of Science and Technology,
South Kensington. [*Received, July 1st*, 1925.]

CCXC.—*Electrometric Studies of the Precipitation of Hydroxides. Part IV. Precipitation of Mercuric, Cadmium, Lead, Silver, Cupric, Uranic, and Ferric Hydroxides by Use of the Oxygen Electrode.*

By Hubert Thomas Stanley Britton.

Attention was directed in Part I (this vol., p. 2110) to the limited applicability of the hydrogen electrode, and consequently resort has been made to the oxygen electrode in order to study the precipitation reactions described in the following pages. Although oxygen electrodes cannot be used to follow with accuracy the changes in hydrogen-ion concentration which may take place during a reaction, they are sufficiently responsive to show the character of the changes and under certain conditions an approximate idea of the hydrogen-ion concentrations may be obtained from the titration curves. The oxygen electrode appears to have been employed for a similar purpose by Ralston (*Trans. Amer. Electrochem. Soc.*, 1923, **43**, 87), who found it of considerable use in the hydrolytic purification of electrolytes, such as the freeing of copper sulphate solutions from ferric hydroxide.

It was shown (Britton, J., 1924, **125**, 1572) in oxygen electrode titrations of chromic acid that, if the hydrogen-ion concentrations were known of solutions at two remote stages of the titration, rough estimates of the p_H of intermediate solutions could be obtained by assuming the voltages to be proportional to the p_H. This method, however, was found later to introduce errors sometimes as great as a whole p_H unit (this vol., p. 1915). The method has been further tested in the present titrations by using solutions which contained a known concentration of free acid, from which the initial p_H could be calculated, and continuing the titrations until the solutions had become alkaline and of known p_H. Table I gives particulars of the solutions titrated and the concentrations of free acid initially present. The titrations were performed with 100 c.c. of solution at 18° in each case by the method described for the previous acid titrations, the normal calomel half-element being used; as junction liquid in titrations 3 and 4 saturated potassium nitrate solution was employed instead of potassium chloride for obvious reasons. Each titration was followed by at least two oxygen electrodes and the solution was kept thoroughly mixed by a rapid current of oxygen, flowing throughout the whole titration.

The curves given by each pair of electrodes were as a rule similar, although by no means coincident, and tended to become closer to

TABLE I.

Titration and curve No.	100 C.c. of solution contained : free acid.	salt.	Sodium hydroxide. Normality.	C.c. for acid.	C.c. for salt.	Total.
1	0·0212*N*-HCl	0·02*M*-$HgCl_2$	0·1018	20·8	39·3	60·1
2	0·0199*N*-H_2SO_4	0·02*M*-$CdSO_4$	0·1018	19·6	39·3	58·9
3	0·0202*N*-HNO_3	0·02*M*-$Pb(NO_3)_2$	0·1005	20·1	39·8	59·9
4	0·0202*N*-HNO_3	0·02*M*-$AgNO_3$	0·1018	19·6	39·3	58·9
5	0·0199*N*-H_2SO_4	0·02*M*-$CuSO_4$	0·1018	19·6	39·3	58·9
6	0·0149*N*-HNO_3	0·00833*M*-$U(NO_3)_6$	0·1005	14·9	49·8	64·7
7	0·0202*N*-HCl	0·0133*M*-$FeCl_3$	0·1005	20·1	39·8	59·9

one another on repeated use; continued use, however, impaired the sensitiveness of the electrodes to changes of hydrion concentration. The differences between the typical *E.M.F.*'s given by the oxygen–normal calomel combination at the beginning and at the end of the titrations, and the corresponding *E.M.F.*'s which ordinarily would have been given by the hydrogen electrode in solutions of identical hydrion concentration, against the normal calomel half-cell, are given in Table II. These differences are, in effect, the *E.M.F.*'s of the oxygen–hydrogen cells set up in the various solutions.

TABLE II.

Titration No.	Solution.	*E.M.F.* of O_2 | solution | H_2 (volts). Beginning.	End.
1	HCl and $HgCl_2$	0·98	1·05
2	H_2SO_4 and $CdSO_4$	1·09	1·08
3	HNO_3 and $Pb(NO_3)_2$	1·04	1·05
4	HNO_3 and $AgNO_3$	0·96	1·13
5	H_2SO_4 and $CuSO_4$	0·94	1·06
6	HNO_3 and $U(NO_3)_6$	0·85	0·96
7	HCl and $FeCl_3$	0·97	1·03

Both the hydrogen-ion concentration and the oxidising agents, which may be undergoing titration, have some influence on the oxygen electrode *E.M.F.* If the latter happens to be either small or almost independent of the hydrogen-ion concentration, then the proportional hydrogen-ion concentration scale may be expected to give a fairly accurate measure of the hydrion concentration. The extrapolated *E.M.F.*'s of the oxygen–hydrogen cell in the case of the uranium nitrate titration are much lower than usual, and it is probable that the small increase in potential difference was uniformly distributed over the whole titration, for the p_H's indicated by the scale at the various stages of the reaction were,

as far as could be ascertained colorimetrically, in approximate agreement. The low potential differences which were obtained in all the uranium titrations had nothing to do with the ageing of the platinum black, as in many instances freshly platinised electrodes were employed. A regular increase in the potential difference of the oxygen–hydrogen cell could not have taken place in the silver nitrate titrations, for according to the proportional hydrion scale the silver oxide was precipitated at p_H 6, whereas calculation from the solubility product of silver hydroxide showed that the true precipitation p_H lay between 9 and 10. By comparing the voltage actually observed when the precipitation began, 0·4 volt, with that which would be given by a hydrogen electrode indicating p_H 9, each compared with the normal calomel electrode, the *E.M.F.* of the oxygen–hydrogen cell is found to be 1·21 volts. This value is greater than either the initial (0·96) or the final (1·13) value, and was probably caused by the instability of the silver oxide. The remaining solutions investigated showed much less variation in their extrapolated *P.D.*'s, and when isolated p_H's were found by means of indicators and compared with those given by the scales, they were generally found to agree within half a p_H unit.

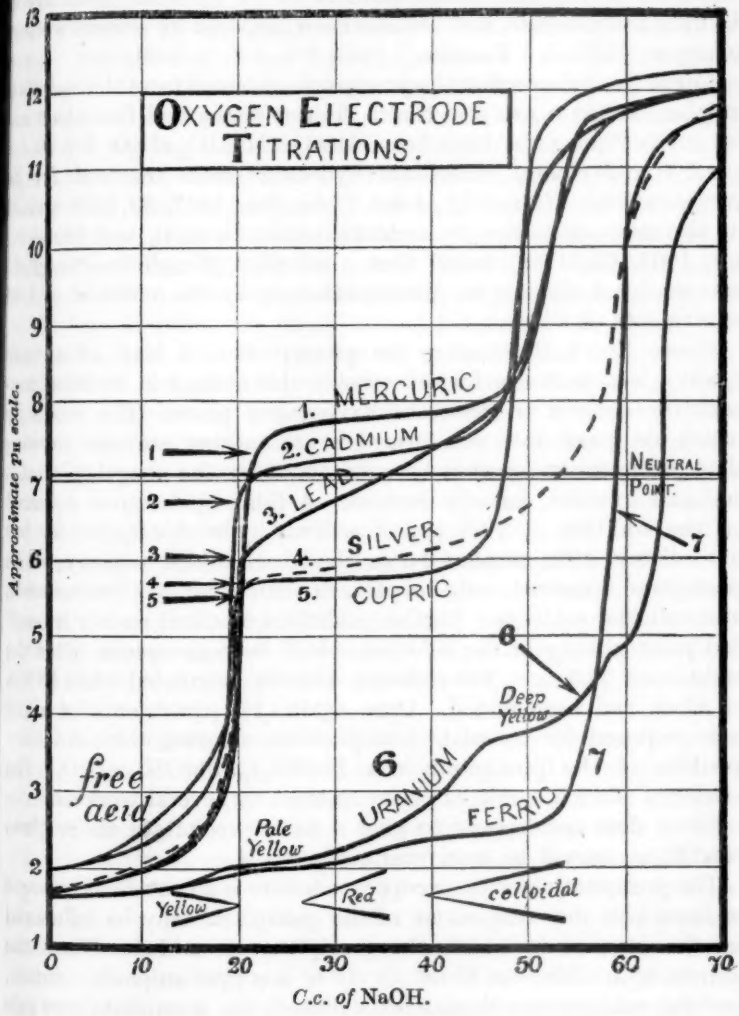
The differences in the actual voltage readings, which covered equal ranges of hydrion concentration, were usually unequal in any two titrations. Thus the change in p_H from 1·7 to 12·0 (say) would be indicated by the hydrogen and normal calomel electrodes by a variation in *E.M.F.* from — 0·381 to — 0·975 volt, a difference of 0·594 volt. In the case of the lead titration, the oxygen electrode *E.M.F.*'s moved over the same range with an almost equal change in voltage, *viz.*, from 0·667 to 0·067, a difference of 0·600 volt. In the other extreme titration, that of silver nitrate, the *E.M.F.* varied from 0·578 to 0·167 volt, a difference of 0·411 volt only.

In order to represent these titrations graphically (Fig. 1), it has been found necessary to convert the observed voltages into the approximate p_H values by simple proportion (this vol., p. 1915); these values are plotted as ordinates, and the number of c.c. of alkali added as abscissæ. Curve No. 4, representing the titration of silver nitrate, is dotted, for, as previously shown, the proportional hydrion scale is inapplicable. The arrows denote the beginning of precipitation.

The precipitation of basic mercuric chloride (curve No. 1) began when p_H 7·4 was attained; the precipitate, at first white, became brown as more alkali was added. Precipitation was complete when three-quarters of the amount of alkali required for the complete decomposition of the mercuric chloride had been added. At this point—50·3 c.c. of sodium hydroxide—the addition of more alkali

aused a rapid increase in p_H. The basic chloride was readily ecomposed on the addition of an excess of alkali. The fact that xactly 1·5 equivalents of sodium hydroxide were sufficient to

FIG. 1.



transform 1 molecule of mercuric chloride completely into an insoluble basic precipitate seems to furnish good evidence that the precipitate first formed was a definite salt, *viz.*, $HgCl_2,3HgO$. Some decomposition took place immediately an excess of alkali was added, for after precipitation was complete about 2 c.c. of

alkali had to be added before the solution attained a marked alkalinity. The partial investigation by Toda (*Memoirs Coll. Sci. Kyoto*, 1921, **4**, 305) of the ternary system HgO–HCl–H_2O at 35° failed to establish the individuality of $HgCl_2,3HgO$. A crystalline basic chloride of this composition is stated to occur naturally as kleinite and mosesite, and has also been prepared by several workers (compare Mellor's "Treatise," 1923, Vol. IV, p. 842).

Curve No. 2 shows that the precipitate obtained from the cadmium sulphate solution was also basic. It was heavy and flocculent and its composition must have been $CdSO_4,3Cd(OH)_2,xH_2O$, for 49 c.c. (= 1·5 equivalents) of sodium hydroxide were required for its precipitation. Harned (*J. Amer. Chem. Soc.*, 1917, **39**, 252) arrived at the same conclusion by conductimetric titration, and Pickering (J., 1907, **91**, 1981) found that a solution of cadmium sulphate was rendered alkaline to phenolphthalein by the addition of 1·46 equivalents of alkali.

Curve No. 3, illustrating the precipitation of lead as a basic nitrate, is remarkable for the considerable change in hydrion concentration which is shown to have taken place. The mode by which the precipitate was formed is yet another example showing that precipitation is often brought about by the coagulation of a colloidal solution, initially formed. A faint opalescence occurred on the addition of 20·5 c.c. of sodium hydroxide ($p_H = 6$), but immediately after another 0·5 c.c. had been added a heavy, white precipitate appeared, only to pass, in the course of a few seconds, into colloidal solution. Further additions of alkali merely intensified the turbidity of the solution, which became opaque after the addition of 33·5 c.c. The colloidal solution coagulated when 38 c.c. of alkali had been added. Once again, 1·5 equivalents of alkali were required for complete precipitation, showing that the composition of the precipitate was $Pb(NO_3)_2,3Pb(OH)_2,xH_2O$. The existence of such a salt has been claimed by several workers.

Silver does not appear to give a basic precipitate under these conditions, as will be seen from curve No. 4.

The precipitation of basic copper sulphate is an excellent example to show how the composition of the precipitate may be influenced by the manner in which the precipitant is added. When the sodium hydroxide was added slowly to a copper sulphate solution, and the solution was thoroughly agitated, the precipitate was pale blue, amorphous, and heavy, but when the alkali was added quickly, no care being taken to ensure thorough mixing, the precipitate was green and gelatinous and, in contrast to the former precipitate, turned black either on standing or on heating. Provided the amount of alkali added was insufficient to render the solution

alkaline, the gelatinous precipitate, on shaking, gradually became converted into the less basic, amorphous precipitate. The precipitate obtained in the titration was amorphous and, as will be concluded from the amount of alkali (1·47 equivalents) required for its precipitation and to render the solution alkaline, contained CuO and SO_3 in the molar ratio 4 : 1. In his experiments on copper sulphate solutions, Pickering (*loc. cit.*) found that whilst 1·53 equivalents of sodium hydroxide actually produced complete precipitation as basic sulphate, the solution on treatment with alkali did not become alkaline to phenolphthalein until about 1·7 equivalents had been added. This initial alkalinity gradually disappeared until approximately 1·8 equivalents had been added. It is evident that Pickering obtained complete precipitation as $CuSO_4,3Cu(OH)_2,xH_2O$ in one case. The fact that the initial alkalinity did not coincide with the end of precipitation was due to the way in which the alkali was added during the testing with phenolphthalein. In the present electrometric titration, complete precipitation and alkalinity to phenolphthalein took place simultaneously. Pickering believed that the greater amount of alkali pointed to the precipitation of a mixture of basic sulphates, $4CuO,SO_3$ and $10CuO,SO_3$; the individuality of the latter he thought to be sufficiently established by the amount of alkali required to cause final alkalinity. Harned (*loc. cit.*), by titrating with a copper electrode, also found that precipitation was complete when 1·7 equivalents of sodium hydroxide had been added. Harned's observation, as was Pickering's, was due to the manner in which the precipitant was added. In a subsequent paper, it will be shown that the pale blue, amorphous precipitate is a definite basic salt, $4CuO,SO_3,4H_2O$.

The uranic solution used in the titration was prepared by dissolving so-called uranyl nitrate in nitric acid. The colour of the solution was pale yellow, but important changes in the intensity occurred during the titration. Curve No. 6 shows that a slight inflexion occurred immediately after the acid in excess of that required to form uranic nitrate had been neutralised with 14·9 c.c. of alkali; this, perhaps, may be due to the presence of sexavalent uranium nitrate in the solution (compare the titrations of the chlorides of zirconium and ferric iron). This small inflexion was repeatedly obtained. No appreciable change in colour was observed until 45 c.c. of sodium hydroxide had been added, the composition of the solute then being $U(NO_3)_{2\cdot38}(OH)_{3\cdot62}$. Thereafter the solution, though remaining clear, gradually became deeper in colour until 55·8 c.c. of alkali had reacted, the solution then containing $U(NO_3)_{1\cdot08}(OH)_{4\cdot92}$; at this stage a yellow precipitate began to

separate. It happened that this change corresponded exactly to a new section of the curve, and the point of inflexion corresponded to the solution in which the change in shade of yellow was first noticed. The diminished hydrion concentrations of the deeply coloured solutions, about p_H 3·7, were close to that at which precipitation began, p_H 4·2. The deepening in colour of the highly basic solutions seems to have been due to a gradual increase in the size of the basic particles, the uranium hydroxide being held in solution in a state closely akin to that of a colloid. The hydrion concentration of the solution when 48 c.c. of alkali had been added was $10^{-3·7}$; the solution then contained the proportions of uranium and nitrate present in uranyl nitrate but was much deeper in colour than that obtained by dissolving uranyl nitrate crystals. The explanation of this difference probably lies in the fact that uranyl nitrate is crystallised from strongly acid solutions. On solution in water, it tends to revert to a state which is probably colloidal, as shown by the changes in colour and in conductivity which it undergoes on standing and especially at higher temperatures (Dittrich, *Z. physikal. Chem.*, 1899, **29**, 449). If the increase in conductivity which takes place on standing is due to the formation of particles which are essentially colloidal, these particles must be capable of some kind of ionisation. There seems to be very little support for the belief that uranyl salt solutions contain the "uranyl" kation; none is to be found in conductivity measurements, which show that the increases in conductivity with dilution of solutions of the nitrate, chloride, and sulphate are anomalous.

The diagram shows that precipitation was complete when 64 c.c. of alkali had been added as compared with the 64·7 c.c. which were required for the complete formation of uranic hydroxide. Hence the precipitate was uranic hydroxide containing a very small quantity of undecomposed nitrate. The text-books state that alkalis precipitate "diuranates" and not uranium hydroxide; *e.g.*, with sodium hydroxide, the precipitate is stated to be $Na_2U_2O_7$ (compare Roscoe and Schorlemmer's "Treatise," Vol. II, p. 1154, revised 1923). Jolibois and Bossuet (*Compt. rend.*, 1922, **174**, 1625) found that the precipitates produced by the action of sodium hydroxide on uranyl nitrate solutions contained no nitrate; the small quantities of sodium hydroxide present, varying from 1·2 to 8% they considered to be adsorbed.

Dilute acid solutions of uranium nitrate or uranyl salt solutions themselves, when gently heated, underwent some profound change; the colour became deeper and the reverse change on cooling took place very slowly. They became alkaline to phenolphthalein when

the theoretical amount of alkali was added, but a precipitate separated only when an appreciable excess of alkali had been added or the solution had been boiled for some time. The opalescence of the alkaline colloidal solution depended on the temperature to which the original solution had been heated. The deep yellow solutions formed by gentle heating were almost clear, whereas those which had been boiled became visibly colloidal. If not too great an excess of alkali had been added, the resulting colloidal solutions remained quite stable for several days. They were coagulable on addition of 1 or 2 c.c. of saturated potassium chloride solution. Heating thus appeared to have caused some change in the state of aggregation of the particles of uranium hydroxide or more likely of highly basic salt, which were probably in equilibrium with free nitrate ions and were thereby enabled to enter into reaction with alkalis so that the uranium hydroxide complexes remained in colloidal solution.

Curve 7 represents the titration of an acid solution of ferric chloride and correlates the changes in hydrion concentration with the changes in colour. It is something more than a coincidence that the colours of solutions containing basic salts should be similar to those of their respective hydroxides. The colour of solutions of both the basic salts of chromium with strong acids and chromium hydroxide is green, and the uranium solutions are pale yellow but become intensely yellow as they become more basic and are then identical in colour with uranium hydroxide. As is well known, ferric chloride solutions freshly prepared or containing an excess of free acid, are only slightly coloured; on standing, the solution reddens and its colour approaches that of red ferric hydroxide. In the present titration the end of the neutralisation of the free acid appears to be indicated by an inflexion, at 20·1 c.c. of sodium hydroxide. As the solution was rendered more basic, the colour gradually changed from yellow to red. It became quite red after addition of 30 c.c. of sodium hydroxide, when the composition of the solute had become $Fe(OH)_{0\cdot74}Cl_{2\cdot26}$, and with 39 c.c. it began to opalesce. Afterwards the solution became increasingly colloidal and became opaque at p_H 3, which, as will be seen from the curve, occurred just when the sudden change in hydrion concentration had begun. Coagulation set in when the p_H had become 6·6 and 58 c.c. of alkali had been added, the composition of the basic chloride then being $Fe(OH)_{2\cdot85}Cl_{0\cdot15}$.

As the colloidal solution persisted until nearly all the chloride had reacted, experiments were made to see if it were possible to prevent coagulation while the solution was being subjected to a sudden fall in hydrion concentration. As in the case of basic

uranium nitrate solutions, this possibility depended on the changes which had taken place in the ferric chloride solutions before treatment with alkali. Aqueous solutions of ferric chloride more dilute than $N/25$, on boiling, acquired a deep red colour, and often remained colloidal on treatment with $N/10$-alkali in slight excess. Small red, amorphous precipitates separated in some cases, but even then the precipitation was incomplete and the solids did not settle until several hours had elapsed. The presence of a little hydrochloric acid in the solutions before heating had some stabilising effect on the colloidal solutions which were subsequently produced. In one case the colloidal solution remained stable for nearly 3 months. This solution was prepared by adding 55 c.c. of $N/10$-sodium hydroxide to 500 c.c. of a boiling solution containing 100 c.c. of $N/25$-ferric chloride and 10 c.c. of $N/10$-hydrochloric acid. It seems certain that the red colour of boiled ferric chloride solutions was due to dispersed ferric hydroxide particles, and consequently the increase in the size of the basic chloride particles caused by rendering the solution alkaline was not so great as that occurring in an unboiled solution, and therefore did not produce coagulation. The increased stability of the colloidal solutions prepared from acidified ferric chloride solutions was probably due to the effect of the acid in suppressing the growth of the colloidal particles on boiling, thereby giving rise to a more highly dispersed and more stable colloidal solution. Prolonged boiling decomposed these alkaline colloidal solutions, and they were readily coagulated on addition of electrolytes in sufficient amounts.

It is probable that the solubility product of very weak bases such as ferric hydroxide has very little meaning, but in view of the recent work of Jellinek and Gordon (*Z. physikal. Chem.*, 1924, **112**, 235) it is interesting to compare their value for $[Fe^{\cdots}][OH']^3$, *viz.*, $10^{-37\cdot9}$, with that given by the titration curve. They measured the hydrogen-ion concentrations with the hydrogen electrode of solutions of ferric chloride, containing potassium chloride to coagulate the colloidal solutions, to which varying amounts of sodium hydroxide had been added. The concentration of ferric ions in the mother-liquor was determined colorimetrically as thiocyanate. The latter method is probably unsatisfactory, because the acid used would materially affect the concentration of ferric ions in a basic ferric chloride solution. If it be assumed that in the titration the appearance of opalescence marked the point at which ferric hydroxide actually began to separate, and that the amount of free ferric ions was equivalent to the remaining amount of alkali to be added to decompose the ferric chloride completely, the value for the solubility product becomes $10^{-37\cdot7}$. Thus opalescence occurred

on the addition of 39 c.c. of $N/10$-alkali; $p_H = 2{\cdot}3$. Hence $[OH'] = 10^{-11{\cdot}8}$ and $[Fe'''] = 20{\cdot}9/39{\cdot}8 \,.\, 100/139 \,.\, 0{\cdot}0133 = 10^{-2{\cdot}3}$. Müller ("Das Eisen und seine Verbindungen," 1917, p. 281) calculated the value $6{\cdot}5 \times 10^{-47}$ from Bodländer's formula (*Z. physikal. Chem.*, 1898, **27**, 66).

Arrangement of Metals in the Order of the Hydrogen-ion Concentrations required for the Precipitation of their Hydroxides.

It was stated in Part I that no principle has yet been found which leads to a satisfactory arrangement of the metals such that the order is that of the basic strengths of their hydroxides. The titrations described in the foregoing pages show that for each hydroxide there is a definite hydrogen-ion concentration at which its precipitation normally takes place. It is true that the majority of the hydroxides are thrown out of solution as basic precipitates, but the hydrogen-ion concentrations at which these are precipitated probably do not differ greatly from those of the particular hydroxides. The table gives the metals in the order of the hydrogen-ion concentrations at which their respective hydroxides are precipitated from dilute solutions. Although it is not certain that this order is that of the actual basic strengths of the hydroxides, it can be stated, as will be shown later, that it is these hydrogen-ion concentration relationships which underlie many of the reactions of the various metallic salt solutions.

Hydrion conc.		Hydrion conc.		Hydrion conc.	
10^{-11}	Magnesium		Cadmium		Copper
10^{-10}			Praseodymium		Chromium
10^{-9}	Silver		Neodymium	10^{-5}	
	Manganous		Yttrium		Aluminium
	Lanthanum	10^{-7}	Samarium	10^{-4}	
	Mercuric		Ferrous (?)		Uranic
10^{-8}	Cerous		Lead (?)		Thorium
	Cobalt	10^{-6}	Zinc	10^{-3}	
	Nickel		Beryllium		Stannous
					Zirconium
					Ferric

An arrangement now widely adopted is that based by Abegg and Bodländer (*Z. anorg. Chem.*, 1899, **20**, 453) on their theory of electroaffinity, which states that the electrolytic potential constitutes an approximate measure of the basic strength of the metal. Comparison with the present arrangement brings out the following important differences. According to the position of aluminium in the table, aluminium hydroxide is an extremely weak base, weaker than chromium hydroxide, yet aluminium occurs higher than chromium in the electropotential series. There is no doubt

that both aluminium and chromium hydroxides are much weaker bases than manganous hydroxide, and this is also indicated by the present scheme, but according to the electropotential series they are both placed above manganese. Heyrovský (*Proc. Roy. Soc.*, 1923, *A*, **102**, 628) has pointed out that the thallous potential is small, which necessitates placing thallium relatively close to hydrogen in the electropotential series, in spite of the fact that thallous hydroxide is a strong base and is not precipitated by alkalis. If it be assumed that the electrolytic potentials of metals under identical conditions are a measure of their electroaffinities, *i.e.*, the free energies by which the elements take up electric charges, it cannot be concluded, as was admitted by Abegg and Bodländer, that the potentials as determined are in any way parallel to the electroaffinities, for nothing is known of the relative atomic solubilities of the various metals in water. Unless it is known that the number of atoms of the different metals which pass into solution is the same, no guarantee can be obtained that an arrangement accruing therefrom is in any way true. Heyrovský attempted to amend the above method by introducing such factors as the mass of the kation, and obtained an order which he stated "comes out right." Heyrovský's system indicates that lead hydroxide is a stronger base than magnesium hydroxide, and that mercuric oxide is a very weak base, weaker than zinc hydroxide. The present table suggests the contrary in both cases. It is well known that water becomes alkaline (to litmus) when shaken with mercuric oxide, but remains neutral when shaken with zinc oxide.

It is probable that the present table provides as satisfactory an arrangement as any that has been hitherto advanced, as far as the general reactions which involve the strength of the base are concerned. The position of the hydroxides in the table is the important factor in processes for separating hydroxides or basic salts, as was shown to be the case in the separation of thoria from the rare earths (see Part III). The basic acetate and basic succinate methods for the separation of manganese from iron depend on the great difference in hydrogen-ion concentration required to precipitate their respective hydroxides. Lundell and Knowles (*J. Amer. Chem. Soc.*, 1923, **45**, 676) have shown that the separation may equally well be performed by fractional precipitation with ammonia in presence of ammonium chloride, the precipitation of the ferric hydroxide being controlled by rendering the solution just alkaline to methyl-red, *i.e.*, about p_H 6·3. The reason for this is apparent from the hydrion table of the hydroxides. The table also explains why mercuric oxide can be used as a separating agent for various bases. Thus E. F. Smith and Heyl (*Z.*

anorg. Chem., 1894, **7**, 87) showed that mercuric oxide caused the complete precipitation in the cold of ferric, aluminium, and chromium hydroxides, the partial precipitation of zinc, cobalt, nickel, uranium, beryllium, cerous, and lanthanum hydroxides, and failed to precipitate manganous hydroxide. The table shows that the hydrogen-ion concentration peculiar to mercuric oxide is greater than that required to precipitate manganous hydroxide, is approximately equal to that required for lanthana, is somewhat less than that required by those hydroxides which were partly precipitated, and is considerably less than that of the three bases which were completely precipitated.

Summary.

(1) The reactions between sodium hydroxide and salt solutions of certain metals have been followed with the oxygen electrode, the hydrogen electrode being inapplicable.

(2) A scale of hydrogen-ion concentrations has been applied to the observed voltages, accurate to the extent of about 0·5 p_H unit except in the case of the silver nitrate titration.

(3) Basic precipitates, probably containing definite basic salts, were obtained from solutions of mercuric chloride, copper sulphate, cadmium sulphate, and lead nitrate.

(4) The precipitate obtained from uranium nitrate solution was the hydroxide containing a little nitrate, and not sodium diuranate as is often stated.

(5) Significant changes in colour were observed in the titrations of both uranic and ferric salts.

(6) The twenty-five hydroxides which have been investigated have been arranged in the order of their respective precipitation hydrogen-ion concentrations.

In conclusion, the author wishes to thank Prof. J. C. Philip, F.R.S., for kindly placing facilities at his disposal, and the Department of Scientific and Industrial Research for a personal grant.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON, S.W. 7. [*Received, July 1st*, 1925.]

CCXCI.—*The Interaction of Ethyl Acetoacetate and o-Hydroxydistyryl Ketones. Part II.*

By ISIDOR MORRIS HEILBRON, THOMAS ALFRED FORSTER, and ABRAHAM BRUCE WHITWORTH.

THE condensation of ethyl acetoacetate with *o*-hydroxydistyryl ketones was shown by Heilbron and Forster (J., 1924, **125**, 2064) to lead to the formation of *cyclo*hexenones and not, as in the case

of the *o*-hydroxymonostyryl derivatives, to pyrones. Further, it was found that the position taken up by the β-ketonic ester in the conjugated system can be arrived at owing to the fact that when it attaches itself to the styryl residue containing the *o*-hydroxyl the resulting *cyclo*hexenone is free of the carbethoxy-group. Thus the interaction of 2′-methoxy-2-hydroxydistyryl ketone with ethyl acetoacetate leads to the formation of two *cyclo*hexenones the structures of which have been proved to be in accord with the following formulæ :

$$\mathrm{HO{\cdot}C_6H_4{\cdot}CH(CH_2{\cdot}CO{\cdot}CH)CH_2{\cdot}C{:}CH{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}OMe} \quad \text{(I.)}$$

$$\mathrm{MeO{\cdot}C_6H_4{\cdot}CH(CO_2Et{\cdot}CH{-}CO{-}CH)CH_2{\cdot}C{:}CH{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}OH} \quad \text{(II.)}$$

In order to test whether *cyclo*hexenone formation is an invariable result of such condensations, the study of this reaction has now been extended to the case of the extremely reactive unsymmetrical 4′-dimethylamino-2-hydroxydistyryl ketone (XIII), in which the greater amount of the free affinity is almost certainly concentrated at C(1) (Heilbron and Buck, J., 1921, **119**, 1500). In consequence of this it was anticipated that ethyl acetoacetate would enter the molecule at positions 1—2 (formula XIII), giving rise to the *cyclo*hexenone (III), if this type of compound were actually formed.

$$\mathrm{HO{\cdot}C_6H_4{\cdot}CH(CH_2{\cdot}CO{\cdot}CH)CH_2{\cdot}C{:}CH{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NMe_2} \quad \text{(III.)}$$

The result obtained was anomalous, for although a *cyclo*hexenone resulted when the reactants were condensed in presence of concentrated aqueous potassium hydroxide, the *cyclo*hexenone contained the original carbethoxy-group, and consequently if the deductions previously arrived at are correct, must represent the compound of structure IV. Now Borsche (*Annalen*, 1910, **375**, 145) has shown that whereas distyryl ketone readily reacts with ethyl acetoacetate in presence of piperidine, *pp*′-tetramethyldiaminodistyryl ketone is unreactive under these conditions. It has now been ascertained that condensation can be brought about under similar conditions to those used in the above experiment, resulting in the formation of the *cyclo*hexenone (V).

$$\mathrm{Me_2N{\cdot}C_6H_4{\cdot}CH(CO_2Et{\cdot}CH{-}CO{-}CH)CH_2{\cdot}C{:}CH{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}OH} \quad \text{(IV.)}$$

$$\mathrm{Me_2N{\cdot}C_6H_4{\cdot}CH(CO_2Et{\cdot}CH{-}CO{-}CH)CH_2{\cdot}C{:}CH{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NMe_2} \quad \text{(V.)}$$

Similarly, by employing 50% potassium hydroxide, 4-dimethylaminostyryl methyl ketone also reacts with ethyl acetoacetate,

iving in the first place the saturated *cyclo*hexane derivative (VI), rom which water can easily be removed with formation of (VII).

$$\underset{\text{(VI.)}}{\begin{matrix}CO_2Et\cdot CH{-}CO{-}CH_2\\ Me_2N\cdot C_6H_4\cdot CH\cdot CH_2\cdot C(OH)Me\end{matrix}} \xrightarrow{-H_2O} \underset{\text{(VII.)}}{\begin{matrix}CO_2Et\cdot CH{-}CO{-}CH\\ Me_2N\cdot C_6H_4\cdot CH\cdot CH_2\cdot CMe\end{matrix}}$$

It is thus apparent that the *p*-dimethylamino-group, although normally acting as a retarding factor, does not necessarily rule out the structure given in (IV). That this truly represents the constitution of the ketone under consideration was finally proved by oxidising the *cyclo*hexenone with potassium permanganate in acetone solution, when salicylic acid was isolated from the decomposition products. That the anomalous behaviour is closely connected with the peculiar activity of the ketone is evident, for, as shown below, it disappears on methylation of the free hydroxyl group, which reaction destroys the activity of the compound (Heilbron and Buck, *loc. cit.*). Further, with 4′-dimethylamino-4-methoxy-2-hydroxydistyryl ketone, in which the "active" properties of the parent ketone are also entirely suppressed (compare Heilbron and Whitworth, J., 1923, **123**, 238), ethyl acetoacetate yields a *cyclo*hexenone with the carbethoxyl eliminated and which consequently must possess the structure (VIII).

$$MeO\cdot(HO)C_6H_3\cdot\underset{\displaystyle CH_2\cdot CO\cdot CH}{CH}\cdot CH_2\cdot C{:}CH{:}CH\cdot C_6H_4\cdot NMe_2 \quad \text{(VIII.)}$$

On the other hand, the isomeric 4′-dimethylamino-3-methoxy-2-hydroxydistyryl ketone and also the 5-methoxy-compound, both of which are "active" (Heilbron and Whitworth, *loc. cit.*), yield as main products of the condensation *cyclo*hexenones similarly constituted to that obtained from 4′-dimethylamino-2-hydroxydistyryl ketone itself.

$$MeO\cdot C_6H_4\cdot\underset{\displaystyle CO_2Et\cdot CH{-}CO{-}CH}{CH}\cdot CH_2\cdot C{:}CH{:}CH\cdot C_6H_4\cdot NMe_2 \quad \text{(IX.)}$$

$$Me_2N\text{----------}\text{----------}OMe \quad \text{(X.)}$$

$$HO\cdot C_6H_4\cdot\underset{\displaystyle CH(CO_2H)_2}{CH}\cdot CH_2\cdot CO\cdot CH{:}CH\cdot C_6H_4\cdot NMe_2 \quad \text{(XI.)}$$

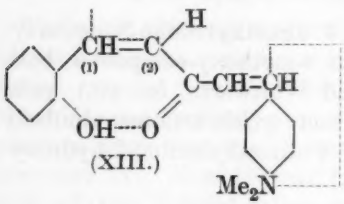
$$Me_2N\text{----------}\text{----------}OH \quad \text{(XII.)}$$

With 4′-dimethylamino-2-methoxydistyryl ketone, two isomeric compounds of empirical formula $C_{26}H_{29}O_4N$ were isolated. The higher-melting *cyclo*hexenone (m. p. 164°), which is only formed in minute amount, was shown to be identical with the methyl ether of (IV) and consequently must possess the structure (X). The isomeride

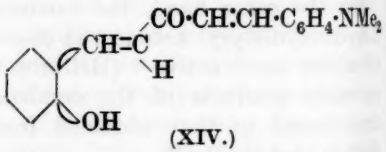
of m. p. 114° must accordingly have the constitution (IX), the reaction in this case having followed the normal course.

The primary object of the investigation has been achieved in definitely proving that, in all the cases examined, *cyclo*hexenones alone are formed as products of the condensation, and the facts harmonise well with the mechanism previously suggested to account for the elimination of carbethoxyl during the condensation (Heilbron and Forster, *loc. cit.*).

As regards the point at which ethyl acetoacetate enters the molecule, this must certainly depend largely on the polar character of the substituent groups and their total effect upon the doubly-conjugated system. The authors feel, however, that the question is too complex to allow of an immediate explanation and that no good purpose would be served by attempting this until the effect of polar influences in less complicated molecules is more thoroughly understood. It is also possible that other factors have to be taken into account and that steric influences play a part in determining the position taken up by the entering group. Thus in the case of 4'-dimethylamino-2-hydroxydistyryl ketone it is conceivable that ethyl acetoacetate, probably through the intermediate formation of a labile addition product, brings about a transformation of the co-ordinated *cis*-form of the ketone (XIII) into a *trans*-isomeride (XIV), a rearrangement which must necessarily modify the distribution of residual affinity effects.



(XIII.)



(XIV.)

This suggestion is supported to some extent by the observation recorded by Heilbron and Buck (*loc. cit.*) that, whereas 4'-dimethylamino-2-hydroxydistyryl ketone is characterised by the ease with which it forms molecular addition compounds and is indeed exceedingly difficult to isolate free from solvate addenda, this may be readily accomplished by crystallisation from ethyl acetoacetate. Again the profound effect which this ester exerts on the configuration of unsaturated ketones is exemplified in the yellow form of *o*-hydroxystyryl methyl ketone, which is readily transformed into its colourless isomeride by crystallisation from this substance (McGookin and Heilbron, J., 1924, **125**, 2099). On the other hand, ethyl cyanoacetate does not induce isomerism of this type (unpublished work)

and it might consequently be expected that in this case addition would take place at the usually reactive unsaturated centre. In presence of 50% sodium hydroxide a condensation product of empirical formula $C_{22}H_{23}O_6N$ was isolated to which either formula (XI) or (XII) could be ascribed. That the former correctly represents the structure of the compound was shown by treatment of the dicarboxylic acid with concentrated potassium hydroxide solution, when fission of the molecule occurred with production of *p*-dimethylaminobenzaldehyde. In considering the formation of this aldehyde, it has to be borne in mind that the effect of the strong alkali might possibly produce a type of reversed Michael reaction, in which case the presence of the *p*-dimethylaminobenzaldehyde would simply result through disintegration of the distyryl ketone, fission occurring at the double bonds. That this, however, was not the case was evident from the fact that no trace of salicylaldehyde was found in the reaction mixture.

EXPERIMENTAL.

Ethyl 3-p-*Dimethylaminophenyl*-5-o-*hydroxystyryl*-Δ^5-cyclo*hexene*-1-*one*-2-*carboxylate* (IV).—A solution containing 4′-dimethylamino-2-hydroxydistyryl ketone (4 g.), ethyl acetoacetate (8 c.c.), absolute alcohol (20 c.c.), and potassium hydroxide solution (3 c.c. of 20%) was allowed to stand at room temperature for 24 hours. The precipitated product (2 g.) was collected and crystallised from either absolute alcohol or benzene. It separates in orange-yellow prisms (m. p. 196°) containing 1 mol. of solvent, from which it can be freed by heating in the steam-oven. It dissolves in concentrated sulphuric acid, giving the deep red solution characteristic of this type of *cyclo*hexenone (Found in material crystallised from alcohol: C, 72·0; H, 7·4; N, 3·1. $C_{25}H_{27}O_4N,C_2H_6O$ requires C, 71·9; H, 7·3; N, 3·1%. Found in material crystallised from benzene: C, 76·8; H, 6·9; N, 2·9. $C_{25}H_{27}O_4N,C_6H_6$ requires C, 77·0; H, 6·9; N, 2·9%. Found in anhydrous compound: C, 73·9; H, 6·7; N, 3·1. $C_{25}H_{27}O_4N$ requires C, 74·1; H, 6·7; N, 3·4%).

Oxidation.—About 1 g. of the substance dissolved in acetone was treated at room temperature with finely-powdered potassium permanganate, added in very small portions at a time. When the oxidation was complete, the mixture was filtered and the residue suspended in water and treated with sulphur dioxide until the manganese dioxide had dissolved. As no solid separated, the solution was made strongly acid with hydrochloric acid and ether-extracted. On removal of solvent, colourless needles were obtained and identified as salicylic acid by mixed m. p. with an authentic specimen of the acid and also by the characteristic ferric chloride coloration.

3-p-*Dimethylaminophenyl*-5-o-*hydroxystyryl*-Δ^5-cyclo*hexene*-1-*one*-2-*carboxylic Acid.*—The previous ester was saponified by heating for 3 hours on the steam-bath with sodium hydroxide solution. The red, pasty mass was dissolved in water, and the acid precipitated by addition of dilute acetic acid. The pure compound crystallised from alcohol in yellow plates, m. p. 225° (Found : C, 73·3; H, 6·0. $C_{23}H_{23}O_4N$ requires C, 73·3; H, 6·1%).

3-p-*Dimethylamino*-5-o-*hydroxystyryl*-Δ^5-cyclo*hexene*-1-*one.*—The free acid was dissolved in glacial acetic acid and boiled for 1 hour with 20% sulphuric acid. After cooling, the green liquid was carefully neutralised with dilute alkali, and the precipitated *cyclo*hexenone crystallised from methyl alcohol, from which it separated in yellow, felted needles, m. p. 232° (Found : C, 78·9; H, 6·9. $C_{22}H_{23}O_2N$ requires C, 79·3; H, 6·9%).

Ethyl 3-p-*Dimethylamino*-5-o-*methoxystyryl*-Δ^5-cyclo*hexene*-1-*one*-2-*carboxylate* (X).—By direct methylation of the corresponding hydroxy-compound by the usual methods, only uncrystallisable products were obtained. The pure methyl ether was readily produced, however, by methylation in acetone solution according to Heilbron and Buck's method (*loc. cit.*). It separates from high-boiling ligroin in lemon-yellow prisms, m. p. 164°, and dissolves in alcoholic potash to a yellow, and in concentrated sulphuric acid to a red solution (Found : C, 74·4; H, 7·0. $C_{26}H_{29}O_4N$ requires C, 74·5; H, 6·9%).

Ethyl 3-o-*Methoxyphenyl*-5-p-*dimethylaminostyryl*-Δ^5-cyclo*hexene*-1-*one*-2-*carboxylate* (IX).—A solution of 4′-dimethylamino-2-methoxydistyryl ketone (3 g.) and 3 c.c. of ethyl acetoacetate in 10 c.c. of alcohol was heated for 3 hours on the steam-bath with potassium hydroxide solution (3 c.c. of 20%), the colour changing from deep red to orange. On gradual dilution with water a semi-solid mass was deposited which proved exceedingly difficult to crystallise, but this was finally accomplished by means of alcohol in presence of animal charcoal. Microscopic examination of the crystals revealed the presence of two substances, which were separated by repeated fractionation from carbon disulphide into a main fraction of the above ester (m. p. 112°) and a small quantity of a substance, m. p. 160°, which was identical with the methyl ether obtained by methylation of the hydroxy-*cyclo*hexenone (IV).

Ethyl 3-o-*methoxyphenyl*-5-p-*dimethylaminostyryl*-Δ^5-cyclo*hexene*-1-*one*-2-*carboxylate* can be conveniently prepared in good yield free from the higher-melting isomeride by treating an alcoholic solution of the ketone (6 g.) and ethyl acetoacetate (8 c.c.) at room temperature with potassium hydroxide solution (6 c.c. of 20%). After a few hours the red solution was inoculated with a crystal of the lower-

melting ether and kept for 2 days. The crude product (5 g.) crystallises from ether in orange needles (m. p. 114°) which are extremely hygroscopic and change colour to brick-red on standing in moist air (Found: C, 74·2; H, 7·2. $C_{26}H_{29}O_4N$ requires C, 74·5; H, 6·9%).

Ethyl 1-*Methoxy*-3-o-*methoxyphenyl*-5-p-*dimethylaminostyryl*-$\Delta^{1:5}$-cyclo*hexadiene*-2-*carboxylate*.—This substance was prepared by dissolving the corresponding *cyclo*hexenone (m. p. 114°) in sodium ethoxide solution and heating under reflux with methyl iodide for 2 hours. It separates from ether in pale yellow needles, m. p. 148° (Found: C, 74·2; H, 7·4. $C_{27}H_{31}O_4N$ requires C, 74·8; H, 7·2%).

Ethyl 3-p-*Dimethylaminophenyl*-5-p-*dimethylaminostyryl*-Δ^5-cyclo*hexene*-1-*one*-2-*carboxylate* (V).—A solution containing 3·2 g. of 4:4′-tetramethyldiaminodistyryl ketone (Sachs and Lewin, *Ber.*, 1902, **35**, 2576), ethyl acetoacetate (5 c.c.), and alcohol (10 c.c.) was heated under reflux for 1 hour with sodium hydroxide solution (1 c.c. of 50%). The clear red liquid was filtered from deposited sodium carbonate, and the *cyclo*hexenone, which separated on cooling, repeatedly crystallised from absolute alcohol. It forms orange-yellow needles, m. p. 174—175°; the *phenylhydrazone* melts at 239° (Found: C, 74·8; H, 7·5; N, 6·7. $C_{27}H_{32}O_3N_2$ requires C, 75·0; H, 7·4; N, 6·5%).

Ethyl 3-p-*Dimethylaminophenyl*-5-*methyl*cyclo*hexane*-5-*ol*-1-*one*-2-*carboxylate* (VI).—A hot alcoholic solution of 4-dimethylamino-styryl methyl ketone (4 g.) and ethyl acetoacetate (6 c.c.) was treated with sodium hydroxide (1 c.c. of 50%), and the resulting red solution kept for 12 hours at room temperature. The *cyclo*hexane crystallises from high-boiling ligroin in colourless needles, m. p. 149° (Found: C, 67·7; H, 8·1; N, 4·4. $C_{18}H_{25}O_4N$ requires C, 67·8; H, 7·9; N, 4·3%). The *phenylhydrazone* separates from absolute alcohol in colourless crystals, m. p. 179° (Found: N, 10·3. $C_{24}H_{31}O_3N_3$ requires N, 10·3%).

Ethyl 3-p-*dimethylaminophenyl*-5-*methyl*-Δ^5-cyclo*hexene*-1-*one*-2-*carboxylate* (VII) is formed on heating an alcoholic solution of the above compound with excess of 10% sodium hydroxide solution, when an oily mass is produced which slowly solidifies. The *cyclo*hexenone crystallises from methyl alcohol after treatment with charcoal in glistening plates, m. p. 66° (Found: N, 4·8. $C_{18}H_{23}O_3N$ requires N, 4·7%).

Ethyl 3-p-*dimethylaminophenyl*-5-(3′-*methoxy*-2′-*hydroxy*)*styryl*-Δ^5-cyclo*hexene*-1-*one*-2-*carboxylate* was prepared by boiling an alcoholic solution of 4′-dimethylamino-3-methoxy-2-hydroxydistyryl ketone (5 g.) and ethyl acetoacetate (2 mols.) for 3 hours under reflux with sodium hydroxide solution (3 c.c. of 40%). After removal of inor-

ganic material by filtration, the crude *cyclo*hexenone was purified by repeated crystallisation first from absolute alcohol and finally from high-boiling ligroin. It forms yellow crystals, m. p. 197–198°, readily soluble in chloroform and benzene, sparingly soluble in alcohol (Found: C, 71·6; H, 6·5. $C_{26}H_{29}O_5N$ requires C, 71·8; H, 6·7%).

3-(4′-*Methoxy*-2′-*hydroxy*)*phenyl*-5-p-*dimethylaminostyryl*-Δ^5-cyclo*hexene*-1-*one*.—An alcoholic solution containing 4′-dimethylamino-4-methoxy-2-hydroxydistyryl ketone (6 g.) and ethyl acetoacetate (8 g.) was heated for ½ hour on the steam-bath with 6 c.c. of 50% sodium hydroxide. After cooling, the solution was filtered from a small quantity of material which could not be further purified, and the filtrate diluted with water. The red, amorphous solid thus obtained was dried and repeatedly crystallised from benzene. The pure *cyclo*hexenone forms orange-red crystals, m. p. 218° (Found: C, 75·8; H, 6·9. $C_{23}H_{25}O_3N$ requires C, 76·0; H, 6·9%).

Ethyl 3-p-*Dimethylaminophenyl*-5-(5′-*methoxy*-2′-*hydroxy*)*styryl*-Δ^5-cyclo*hexene*-1-*one*-2-*carboxylate*.—4′-Dimethylamino-5-methoxy-2-hydroxydistyryl ketone (4 g.) and ethyl acetoacetate (8 g.) were treated in alcoholic solution with aqueous sodium hydroxide (8 c.c. of 20%). After 3 days, the solution was filtered from a small quantity of solid, and the filtrate slowly diluted with water, when the *cyclo*hexenone ester was precipitated. It crystallises from benzene with 1 mol. of solvent of crystallisation in yellow crystals, m. p. 196—197° (Found: C, 74·9; H, 7·2. $C_{26}H_{29}O_5N,C_6H_6$ requires C, 74·8; H, 6·8%). The residue was washed with water to remove inorganic material and crystallised from aqueous pyridine. It separated in orange crystals, m. p. 250°. Analysis of this compound shows that the carbethoxyl has been split off, from which it follows that its structure corresponds to 3-(5′-methoxy-2′-hydroxy)-phenyl-5-*p*-dimethylaminostyryl-Δ^5-*cyclo*hexene-1-one (Found: C, 75·9; H, 6·9. $C_{23}H_{25}O_3N$ requires C, 76·0; H, 6·9%).

γ-p-*Dimethylaminocinnamoyl*-β-o-*hydroxyphenylpropane*-αα′-*dicarboxylic Acid* (XI).—A mixture containing 4′-dimethylamino-2-hydroxydistyryl ketone (8·2 g. of chloroform addition product) and 8 c.c. of ethyl cyanoacetate in 25 c.c. of hot alcohol was treated with sodium hydroxide solution (8 c.c. of 50%), when a deep red coloration rapidly developed and ammonia was evolved. After 16 hours the reaction mixture was filtered from tarry and inorganic material, diluted to 2000 c.c., and the clear orange-red solution rendered acid with dilute acetic acid. As an examination of the precipitated product after crystallisation from benzene indicated that two substances were present, the whole was boiled with sodium hydroxide solution until all evolution of ammonia had ceased. After again

rendering acid, the precipitated product was purified by repeated crystallisation from nitrobenzene, when glistening, orange needles, m. p. 220°, were obtained (Found: C, 66·3; H, 5·8. $C_{22}H_{23}O_6N$ requires C, 66·5; H, 5·8%). That the ethyl cyanoacetate had entered the molecule at positions 1 and 2 (XIII) was proved by slowly running a concentrated alkaline solution of the acid from a dropping-funnel on to boiling potassium hydroxide solution (50 c.c. of 70%) contained in a distillation flask, fitted with a condenser. Pale green crystals (m. p. 66°) separated from the collected steam distillate and were identified as *p*-dimethylaminobenzaldehyde by mixed m. p. determinations with an authentic specimen and by the formation of the phenylhydrazone. The residue left in the flask was carefully examined for the presence of salicylaldehyde, but no trace either of this or of salicylic acid could be found.

The authors desire to thank the Council of the Department of Scientific and Industrial Research for a grant in aid to one of them (T. A. F.) which has enabled this work to be carried out.

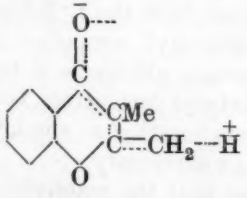
THE UNIVERSITY, LIVERPOOL. [*Received, July 10th,* 1925.]

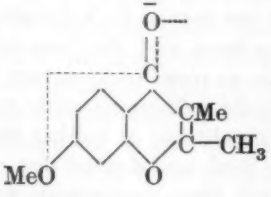
CCXCII.—*Chemical Reactivity and Conjugation. Part II. The Reactivity of the 2-Methyl Group in the 4-Quinazolone Series.*

By ISIDOR MORRIS HEILBRON, FRANCIS NOEL KITCHEN, EDWARD BURDON PARKES, and GEORGE DONALD SUTTON.

It has previously been demonstrated (Heilbron, Barnes, and Morton, J., 1923, **123**, 2559) that the reactivity of the 2-methyl group in 2 : 3-dimethylchromone is conditioned by its capacity to pass into the activated polarised form (I) and that this effect can be entirely suppressed by replacement of hydrogen for methoxyl in position 7, the substituted 7-methoxy-2 : 3-dimethylchromone (II) being entirely unreactive owing to neutralisation of partial valency forces.

(I.)



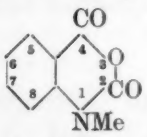


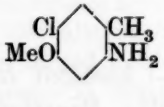
(II.)

The examination of this phenomenon has now been extended to the 4-quinazolone series, which has been widely investigated by

Bogert and his collaborators. That 2 : 3-dimethyl-4-quinazolone (V) contains a reactive methyl group has been demonstrated by the preparation of 2-styryl-3-methyl-4-quinazolone (Bogert, Beal, and Amend, *J. Amer. Chem. Soc.*, 1910, **32**, 1654) and we have now been able to show that the isomeric 1 : 2-dimethyl-4-quinazolone (VI) also is capable of yielding styryl derivatives.

This latter compound was first prepared by Weddige (*J. pr. Chem.*, 1887, **36**, 152) by direct methylation of anthranilamide followed by acetylation and subsequent loss of water from the acetyl methyl derivative. On testing this method, it was found that the yield of methylanthranilamide produced was poor owing to simultaneous formation of anthranilamide dimethyl ether. Other methods were therefore sought, starting from methylanthranilic acid itself. As distillation of the ammonium salt failed to yield the amide, an attempt was made to obtain the 1 : 2-dimethyl-4-quinazolone directly by distillation of the ammonium salt of acetylmethylanthranilic acid, but although some of the desired substance was obtained the yield was again unsatisfactory.

(III.) 



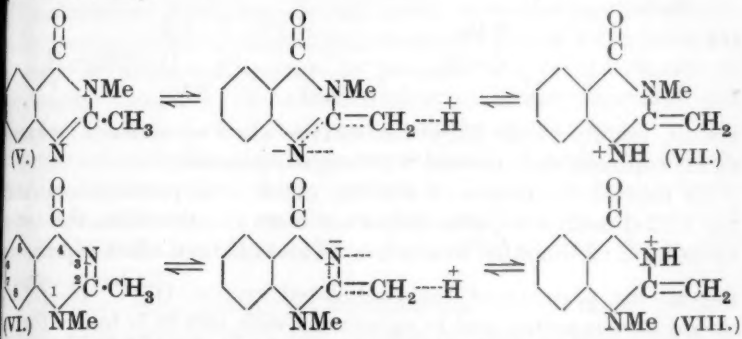
(IV.)

As these methods failed to give the required amide, attention was next directed to an investigation of Niementowski and Rozanski (*Ber.*, 1889, **22**, 1672), who found that isatoic anhydride was readily converted into anthranilamide by 0·88 ammonia. The preparation of methylisatoic anhydride (III) proved a simple matter, a quantitative yield of this substance being obtained on treatment of methylanthranilic acid successively with chloroformic ester and acetyl chloride (compare Bredt and Hof, *Ber.*, 1900, **33**, 27). With concentrated ammonia, it passes readily into methylanthranilamide, a reaction which incidentally furnishes fresh proof of the correctness of the anhydride structure of isatoic acid (compare Erdmann, *Ber.*, 1899, **32**, 2159).

As in the case of 2 : 3-dimethylchromone, both the 1 : 2-dimethyl-4-quinazolone and the isomeric 2 : 3-dimethyl compound readily condense at room temperature with aromatic aldehydes in presence of alcoholic sodium ethoxide to yield 2-styryl derivatives, the more drastic conditions of boiling the reactants together as employed by Bogert, Beal, and Amend (*loc. cit.*) being unnecessary.

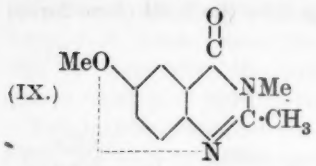
In both these compounds we consider that the reactivity of the methyl group is conditioned by the tendency of the unsaturated nitrogen atoms, as with the carbonyl oxygen atom of 2 : 3-dimethyl-

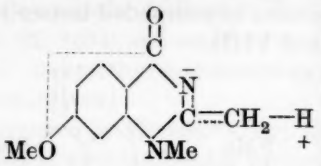
chromone, to acquire a slight negative charge, thus producing an activated phase of the molecule which, in its final state, may be represented as completed isomeric change into the methylene forms (VII and VIII).



It will be observed that in the case of VI a conjugated system, analogous to that contained in 2 : 3-dimethylchromone, is present and it is thus conceivable that, if the activity is conditioned by the presence of this system, substitution of methoxyl for hydrogen in the 7-position might be capable of suppressing the reactivity of the 2-methyl group owing to neutralisation of valency forces. In order experimentally to test this point, 7-methoxy-1 : 2-dimethyl-4-quinazolone was prepared from 4-methoxyanthranilic acid (Ullmann and Dootson, *Ber.*, 1918, **51**, 9) by a series of reactions similar to those detailed in the preparation of the unsubstituted 1 : 2-dimethyl-4-quinazolone. On treatment of this compound with piperonal in presence of alcoholic sodium ethoxide a styryl derivative was readily formed, thus showing that the reactivity of the 2-methyl group in this case is dependent mainly on the activation of the nitrogen atom in position 3. 7-Methoxy-2 : 3-dimethyl-4-quinazolone has also been prepared and, as was to be anticipated, proved to be a reactive substance, the reactivity in this case being conditioned by the nitrogen atom in position 1. An examination of the formula representing the polarised form of 2 : 3-dimethyl-4-quinazolone reveals the fact that in the case of 6-methoxy-2 : 3-dimethyl-4-quinazolone there is a possibility of complete neutralisation of valency forces being effected (IX), and if this occurred the nitrogen atom in position 1 would be rendered inactive. The preparation of this compound and also the isomeric 6-methoxy-1 : 2-dimethyl-4-quinazolone was carried out as described in the experimental portion. Under no conditions, however, could 6-methoxy-2 : 3-dimethyl-4-quinazolone be induced to condense with aromatic aldehydes, the compound being recovered unchanged even when the reactants were heated to high temperatures in presence of a con-

densing agent. On the other hand, 6-methoxy-1 : 2-dimethyl-4-quinazolone, which is incapable of forming a closed valency





circuit, readily yields styryl derivatives when an alcoholic solution of the components is treated with sodium ethoxide.

As regards the degree of activity noted, it appears general that the 1 : 2-dimethyl-4-quinazolones are more reactive than the corresponding 2 : 3-dimethyl isomerides. This enhanced effect is probably due to the presence of the conjugated system $O{=}C{-}N{=}C{\cdot}CH_3$ in the former series, and in agreement with this it is found that a certain retardation of activity is noticeable in the case of 7-methoxy-1 : 2-dimethyl-4-quinazolone, thus showing that neutralisation effects (X), although not sufficient to prevent reaction, do nevertheless come into play.

An interesting point worthy of record was noted during the preparation of 4-methoxyanthranilic acid from *o*-nitro-*p*-cresol methyl ether. Ullmann and Dootson recommend direct oxidation of this compound to the corresponding 2-nitro-4-methoxybenzoic acid with subsequent reduction to the anthranilic acid. As this method is somewhat laborious, attempts were made first to reduce the nitrocresol methyl ether to the amino-compound and then to oxidise the acetylamino-derivative to the acid as detailed by Friedländer, Buchner, and Deutsch (*Annalen*, 1912, **388**, 44). *o*-Amino-*p*-cresol methyl ether was first prepared by Knecht (*Annalen*, 1882, **215**, 83) by reduction of *o*-nitro-*p*-cresol methyl ether with tin and hydrochloric acid and described as a colourless solid, m. p. 47°. On repeating this experiment, an amine (m. p. 112°) was obtained from the steam distillate, which after recrystallisation melted at 116°, and was apparently identical with the compound, m. p. 111°, originally obtained by Limpach (*Ber.*, 1889, **22**, 791; 1891, **24**, 4136). On examination of this substance, we found that it is actually a chlorinated amine to which the constitution IV has been assigned, the reaction obviously having followed a similar course to that occurring during the reduction of *p*-nitrophenetole under similar conditions (Hurst and Thorpe, J., 1915, **107**, 924).

Experimental.

2 : 3-*Dimethyl*-4-*quinazolone* was prepared in good yield by treatment of acetanthranil with methylamine solution according to

Bogert and Seil's method (*J. Amer. Chem. Soc.*, 1907, **29**, 529). It forms colourless needles (from water) containing 1 mol. of solvent, m. p. 72°. The anhydrous compound is obtained by heating in the steam-oven and melts at 112°.

Condensation Products.—In all cases, unless otherwise stated, these were prepared by allowing an alcoholic solution of the reactants to stand at room temperature in presence of sodium ethoxide as condensing agent. The styryl derivative either separates out directly from the alcoholic solution or on dilution with water.

2-Styryl-3-methyl-4-quinazolone was originally prepared by Bogert, Beal, and Amend (*loc. cit.*) by boiling 2 : 3-dimethyl-4-quinazolone with benzaldehyde. It is also readily produced by the method described above and forms pale yellow, silky needles, m. p. 167° (Bogert gives 170°).

4'-Methoxy-2-styryl-3-methyl-4-quinazolone forms bright yellow needles from alcohol, m. p. 146°, soluble in dilute hydrochloric acid, giving an orange-coloured solution (Found : N, 9·5. $C_{18}H_{16}O_2N_2$ requires N, 9·6%).

3' : 4'-Dimethoxy-2-styryl-3-methyl-4-quinazolone separates in yellow plates from benzene, m. p. 208° (Found : N, 8·6. $C_{19}H_{18}O_3N_2$ requires N, 8·7%).

3' : 4'-Methylenedioxy-2-styryl-3-methyl-4-quinazolone forms bright yellow needles, m. p. 185° (Found : N, 9·0. $C_{18}H_{14}O_3N_2$ requires N, 9·2%).

4'-Dimethylamino-2-styryl-3-methyl-4-quinazolone crystallises from alcohol in orange-red needles, m. p. 175°. The solution in dilute hydrochloric acid is dark red (Found : N, 13·8. $C_{19}H_{19}ON_3$ requires N, 13·8%).

Methylisatoic anhydride was produced from methylanthranilic acid according to the method employed by Bredt and Hof (*loc. cit.*) for the production of isatoic anhydride. The acid was refluxed with chloroformic ester (3 mols.) until a clear solution resulted, after which a slight excess of acetyl chloride was added and the heating continued until all evolution of hydrogen chloride had ceased. On cooling, *methylisatoic anhydride* separated in quantitative yield in colourless prisms, m. p. 180° (Found : N, 7·9. $C_9H_7O_3N$ requires N, 7·9%).

The *carbethoxy*-derivative of methylanthranilic acid forms colourless crystals, m. p. 108° (Found : N, 6·4. $C_{11}H_{13}O_4N$ requires N, 6·3%).

Methylanthranilamide was produced in quantitative yield by boiling methylisatoic anhydride with 0·88 ammonia. The thick, white precipitate was filtered off and crystallised from alcohol, from which the pure amide separated in colourless needles, m. p. 162°.

1 : 2-*Dimethyl-4-quinazolone* was obtained in excellent yield by

boiling *N*-methylanthranilamide with excess of acetic anhydride until the volume of the solution had been reduced to about one-half, after which it was diluted with water, rendered alkaline, and again boiled for about 10 minutes. The crude quinazolone separated on cooling and was purified by crystallisation from water, forming silky needles containing water of crystallisation. The anhydrous compound (m. p. 203°) is obtained by heating in the steam-oven (Weddige gives 199°).

2-*Styryl*-1-*methyl*-4-*quinazolone* crystallises from aqueous alcohol in cream-coloured needles, m. p. 245° (Found : N, 10·8. $C_{16}H_{13}ON_2$ requires N, 10·7%).

4′-*Methoxy*-2-*styryl*-1-*methyl*-4-*quinazolone* forms bright yellow needles from aqueous alcohol, m. p. 94°, containing $2H_2O$. The anhydrous compound melts at 156° and dissolves in dilute hydrochloric acid with a deep yellow colour (Found : N, 9·6%). 3′ : 4′-*Methylenedioxy*-2-*styryl*-1-*methyl*-4-*quinazolone* forms yellow needles, m. p. 264° (Found : N, 9·1%). 4′-*Dimethylamino*-2-*styryl*-1-*methyl*-4-*quinazolone* forms orange needles, m. p. 274°. The solution in dilute hydrochloric acid is bright red (Found : N, 13·7%).

6-*Nitro*-3-*hydroxybenzaldehyde*.—*m*-Hydroxybenzaldehyde was nitrated as detailed by Pschorr (*Annalen*, 1912, **391**, 28). The crude nitration product was boiled under reflux with four times its weight of benzene for ½ hour, allowed to cool to 50°, and rapidly filtered. Employing this temperature instead of the lower temperature of 45° used by Pschorr rendered the separation much more complete. 6-Nitro-3-hydroxybenzaldehyde * separates from boiling water in long, yellow needles, m. p. 166° (yield 34% of theory).

6-*Nitro*-3-*methoxybenzaldehyde* was originally obtained by Pschorr, but no details of his method are given. A 95% yield of the ether is readily obtained by the following procedure : 6-Nitro-3-hydroxybenzaldehyde (50 g.) was dissolved in the calculated amount of potassium hydroxide solution and warmed at 60°, after which methyl sulphate (56 c.c.) was added and the mixture well shaken. After cooling, the solution was made alkaline; the methyl ether, which rapidly separated, crystallised from alcohol in colourless needles, m. p. 82°.

6-*Nitro*-3-*methoxybenzoic Acid*.—The oxidation of the aldehyde was carried out by suspending it (20 g.) in 1500 c.c. of warm dilute potassium hydroxide solution (1 mol. KOH) and gradually adding the calculated amount of a 2% solution of potassium permanganate, the whole being mechanically stirred. The alkaline filtrate was

* The preparation of this compound in good yield (87%) has been much simplified by Mason (this vol., p. 1195), whose paper appeared after the completion of the work described in this communication.

rendered acid, the solution saturated with salt and ether-extracted. After removal of solvent the crude acid was crystallised from alcohol, separating in colourless needles, m. p. 97° (yield 87%). It is essential to employ the pure aldehyde in this oxidation, otherwise the yield of acid is largely reduced. This substance was found to contain 1 mol. of water of crystallisation, the anhydrous acid which is obtained by heating in the steam-oven melting at 133° as given by Pschorr.

5-*Methoxyanthranilic acid* was prepared by Pschorr (*loc. cit.*) by reduction of the nitro-acid with ferrous sulphate and ammonia. A more satisfactory method is to carry out the reduction by means of stannous chloride and concentrated hydrochloric acid, when a 75% yield of the required acid results.

5-*Methoxyacetanthranil*.—The method employed was similar to that described by Bogert (*J. Amer. Chem. Soc.*, 1911, **33**, 949). 5-Methoxyanthranilic acid was gradually added to excess of boiling acetic anhydride, when a vigorous reaction occurred with precipitation of a yellow solid which dissolved on further heating. On allowing the solution to cool, the anthranil was deposited in quantitative yield. It crystallises from benzene in colourless, prismatic needles, m. p. 124° (Found : N, 7·5. $C_{10}H_9O_3N$ requires N, 7·3%).

6-*Methoxy*-2-*methyl*-4-*quinazolone*.—On boiling the anthranil for 1 hour under reflux with a large excess of 0·88 ammonia, it gradually dissolved and as the reaction proceeded the quinazolone separated out. It forms glistening needles (from aqueous alcohol), m. p. 270° (Found : N, 14·7. $C_9H_{10}O_2N_2$ requires N, 14·7%).

6-*Methoxy*-2 : 3-*dimethyl*-4-*quinazolone* was prepared in an analogous manner by employing alcoholic methylamine solution and was also easily obtained by the action of methyl sulphate on an alkaline solution of the 2-methylquinazolone. It separates from boiling water in colourless needles containing 1 mol. H_2O, m. p. 87°. The anhydrous compound is readily formed on heating the hydrated substance in a steam-oven and melts at 133° (Found : N, 13·9. $C_{11}H_{12}O_2N_2$ requires N, 13·7%).

Attempts were made to condense this quinazolone with aromatic aldehydes by condensation in presence of alcoholic sodium ethoxide both in the cold and heat, but in each case unchanged substance was recovered. The quinazolone was also heated with piperonal alone under precisely similar conditions to those employed by Bogert (*loc. cit.*), but on extracting the melt practically the whole of it was recovered unchanged. This experiment was repeated in presence of zinc chloride as condensing agent, but here again unchanged quinazolone was obtained.

5-*Methoxymethylanthranilic acid* was prepared according to

Willstätter and Kahn's method (*Ber.*, 1904, **37**, 408) by direct methylation of the sodium salt of the acid with methyl sulphate in the cold. It separates from benzene after treatment with animal charcoal in yellow needles, m. p. 163°. Both the ethereal and the aqueous solution exhibit a strong blue fluorescence (Found: N, 7·7. $C_9H_{11}O_3N$ requires N, 7·7%).

6-*Methoxymethylisatoic anhydride* was prepared as previously described. It crystallises from acetone in colourless needles, m. p. 233° (Found: N, 6·6. $C_{10}H_9O_4N$ requires N, 6·8%). On refluxing with excess of 0·88 ammonia, it is converted into 5-*methoxymethylanthranilamide*, which separates from boiling water in colourless needles, m. p. 145° (Found: N, 15·5. $C_9H_{12}O_2N_2$ requires N, 15·6%).

6-*Methoxy*-1 : 2-*dimethyl*-4-*quinazolone*.—On treatment of the amide with acetic anhydride as described in the preparation of the unsubstituted 1 : 2-dimethyl-4-quinazolone, it is quantitatively converted into 6-methoxy-1 : 2-dimethyl-4-quinazolone, which crystallises from water in long, colourless needles, m. p. 220° (Found: N, 13·8%).

6-*Methoxy*-3′ : 4′-*methylenedioxy*-2-*styryl*-1-*methyl*-4-*quinazolone*.—Unlike the inactive isomeric 6-methoxy-2 : 3-dimethyl-4-quinazolone, the 1 : 2-dimethyl compound reacts readily with aromatic aldehydes, the condensation with piperonal being completed in the cold after 12 hours. By warming on the water-bath the reaction is much accelerated, the condensation product commencing to separate after 10 minutes. The crude product was purified by recrystallisation from alcohol and formed microscopic, yellow needles, m. p. 284° (Found: N, 8·2. $C_{19}H_{16}O_4N_2$ requires N, 8·3%).

4-*Methoxymethylanthranilic acid* was prepared from 4-methoxyanthranilic acid by direct methylation with methyl sulphate. It separates from alcohol in colourless needles, m. p. 165° (Found: N, 7·8%). The conversion of this acid into 7-*methoxymethylisatoic anhydride* follows the directions previously given. The substance crystallises from acetone in colourless prisms, m. p. 200° (Found: N, 6·9%). On treatment with 0·88 ammonia it is quantitatively converted into 4-*methoxymethylanthranilamide*, which crystallises from alcohol in colourless needles, m. p. 138° (Found: N, 15·6%).

7-*Methoxy*-1 : 2-*dimethyl*-4-*quinazolone* was prepared in an analogous manner to that of the isomeric 6-methoxy-compound, and after treatment with animal charcoal separated from absolute alcohol in colourless crystals, m. p. 193°. It crystallises from water with 1 mol. H_2O and melts indefinitely at about 135° (Found: N, 12·6. $C_{11}H_{12}O_2N_2$, H_2O requires N, 12·6%).

7-*Methoxy*-3′ : 4′-*methylenedioxy*-2-*styryl*-1-*methyl*-4-*quinazolone* forms yellow needles (from ethyl alcohol), m. p. 280° (Found: N, 8·3%).

7-Methoxy-4′-dimethylamino-2-styryl-1-methyl-4-quinazolone is best prepared by refluxing an alcoholic solution of the constituents in presence of sodium ethoxide and precipitating the styryl derivative with water. It separates from alcohol in bright red cubes, m. p. 266° (Found : N, 12·8. $C_{20}H_{19}O_2N_3$ requires N, 12·5%).

4-Methoxyacetanthranil, prepared by boiling 4-methoxyanthranilic acid with excess of acetic anhydride, crystallises from water in colourless needles, m. p. 128° (Found : N, 7·4%).

7-Methoxy-2-methyl-4-quinazolone prepared by the usual method crystallises from alcohol in colourless needles, m. p. 272° (Found : N, 14·6. $C_{10}H_{10}O_2N_2$ requires N, 14·7%). On treatment with methyl sulphate it is immediately converted into *7-methoxy-2 : 3-dimethyl-4-quinazolone*. This substance is equally readily prepared by the direct treatment of 4-methoxyacetanthranil with methylamine solution, a reaction which definitely fixes its constitution. The quinazolone crystallises from water with 1 mol. H_2O in colourless needles, m. p. 80°. The anhydrous compound melts at 149° (Found : N, 13·7. $C_{11}H_{12}O_2N_2$ requires N, 13·7%).

7-Methoxy-3′ : 4′-methylenedioxy-2-styryl-3-methyl-4-quinazolone separates from alcohol in yellow crystals, m. p. 193° (Found : N, 8·3%).

5-Chloro-2-amino-4-methoxytoluene.—*o*-Nitro-*p*-cresol methyl ether was reduced by warming with tin and concentrated hydrochloric acid in the usual manner, the solution diluted with water, rendered alkaline, and subjected to steam distillation. The amine (m. p. 112°) crystallised from benzene in colourless plates, m. p. 116° (Found : N, 8·5. $C_8H_{10}ONCl$ requires N, 8·2%). The *acetyl* derivative melts at 183—184° (Found : N, 6·8. $C_{10}H_{12}O_2NCl$ requires N, 6·6%).

In conclusion, we desire to thank the Directors of the United Alkali Company for a grant to one of us (F.N.K.) which has enabled this work to be carried out.

THE UNIVERSITY, LIVERPOOL. [*Received, July 10th*, 1925.]

NOTES.

Preparation of the Phenylcarbamyl Derivatives of Nitrophenols.

By OSCAR L. BRADY and JACK HARRIS.

NITROPHENOLS do not react readily with phenylcarbimide and the following method for the preparation of their phenylcarbamyl derivatives is an improvement on those previously described (Gumpert, *J. pr. Chem.*, 1885, **32**, 278; Michael and Cobb, *Annalen*,